Polyhedron 30 (2011) 93-97

Contents lists available at ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Silver(I) catalyzed oxidation of thiocarboxylic acids into the corresponding disulfides and synthesis of some new Ag(I) complexes of thiophene-2-thiocarboxylate

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ARTICLE INFO

Article history: Received 22 June 2010 Accepted 24 September 2010 Available online 7 October 2010

Keywords: Thioacid Disulfide Silver catalyzed Catalytic oxidation Thiocarboxylate

1. Introduction

Oxidation of thiols into disulfides is an important reaction in biological systems. Several cellular redox potentials are controlled by oxidation of thiols to prevent oxidative damage of proteins. During past two decades a number of reactions have been reported by which thiols can be oxidized to disulfides. Various reagents and oxidants have been employed for conversion of thiols to disulfides [1–3]. Besides enzymatic [4] and electrochemical [5,6] methods a number of such reactions are reported which are catalysed by various transition metals ions [7,8]. Interestingly, similar catalytic reactions converting thiocarboxylic acids into corresponding disulfides are not available in literature. Though cuprous thiobenzoate has been reported [9] to decompose on prolonged heating giving dibenzoyldisulfide along with some other products but the oxidation of thiobenzoate anion is non-catalytic in this process.

We have reported earlier [10] that thioacetic and thiobenzoic acids are converted to diacetyl and dibenzoyl sulfides respectively in presence of In^{3+} . However, these reactions are stoichiometric and give highly stable metal sulfide complexes at the end which can not be dissociated easily to give back the free metal ions to catalyze the reactions in a second cycle. We here report the oxidation of thiobenzoic and thiophene-2-carboxylic acids into the corresponding disulfides using a Ag⁺ salt.

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ABSTRACT

Aromatic thiocarboxylic acids in presence of a base on treatment with silver nitrate under ambient conditions were oxidized to the corresponding disulfides. The reactions were found to be catalyzed by Ag⁺ ions. The catalytic oxidation is paralleled by the Ag(SCOAr) complex formation reaction which could be considerably subsided by adjustment of the reaction conditions. Attempts to use $[Ag(PPh_3)_2]^+$ or $[Ag(PPh_3)]^+$ ion as the catalyst were unsuccessful as these resulted in the formation of the corresponding thiocarboxylate complexes. The products, ArCOSSCOAr (1, 2), $[Ag(SCOAr)(PPh_3)_2]$ (3, 4) and $[Ag(S-COAr)(PPh_3)_4]$ (5) (Ar = C₆H₅, C₄H₃S) were characterized by single crystal X-ray analysis. Compounds 3 and 4 are monomeric while 5 is a cyclic tetramer in the crystalline phase.

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2. Experimental

All the solvents (LR grade) were distilled before they were used. AgNO₃ (Qualigens), thiobenzoic acid and thiophene-2-carbonyl chloride (Sigma–Aldrich) were used as received. Thiophene-2thiocarboxylic acid was synthesized as reported earlier [11]. Triethylamine was stored over NaOH and distilled prior to its use. During the manipulations care was taken to protect the reaction vessels from direct day light. Elemental analyses were carried out by using Exeter Model CE-440 CHN analyzer. IR spectra were recorded as KBr pellets on a VARIAN 3100 FT-IR spectrophotometer in the region 400–4000 cm⁻¹. ¹H and ¹³C NMR spectra were recorded on a JEOL AL300 FT NMR Model spectrometer in CDCl₃ solvent; the chemical shifts were measured with reference to tetramethylsilane (¹H).

2.1. Catalytic oxidation of thiobenzoic acid

To a solution of thiobenzoic acid (0.552 g, 4 mmol) in 10 mL methanol was added a methanolic solution (10 mL) of triethylamine (0.404 g, 4 mmol). After stirring for 30 min, 10 mL of the reaction mixture was added drop wise to a magnetically stirred solution of silver nitrate (0.085 g, 0.5 mmol) in \sim 15 ml methanol. After stirring the reaction mixture for 1 h at 30 °C the remaining portion (10 mL) of the triethylammonium thiobenzoate solution was added into it slowly. The reaction mixture was stirred overnight and then filtered off the black precipitate formed.



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Compound	1	2	3	4	5
Empirical formula	C14H10O2S2	$C_{10}H_6O_2S_4$	C ₄₃ H ₃₅ O ₁ S ₁ P ₂ Ag	$C_{43}H_{35}AgC_{16}O_{3}P_{2}S_{2}$	C ₉₂ H ₇₂ Ag ₄ O ₄ P ₄ S
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	ΡĪ
a (Å)	12.2167(8)	7.9678(3)	10.229(2)	10.398(5)	13.256(6)
b (Å)	12.0017(8)	6.5494(3)	13.210(3)	25.701(5)	14.1978(17)
c (Å)	8.9366(6)	23.1681(11)	14.232(3)	18.721(5)	14.201(2)
α (°)			89.02(3)		60.208(14)
β(°)	107.462(1)	9098.014(4)	76.63(3)	104.937(5)	71.03(2)
γ (°)			76.82(3)		68.88(2)
$V(Å^3)$	1249.91(14)	1197.20(9)	1820.3(6)	4834(3)	2128.3(10)
Ζ	4	4	2	4	1
D_{calc} (g/cm ³)	1.458	1.589	1.404	1.438	1.602
F(000)	568	584.0	788	2112	1290
Temperature (K)	100	293	293	293	150
Collected reflections	8032	4743	7086	30172	16228
Unique reflections	3076	2612	6312	10987	9450
R	0.0551	0.0591	0.0268	0.1162	0.0393
Goodness-of-fit (GOF)	1.16	1.047	1.071	1.030	1.013

Table 1	
Crystallographic data of compounds	1-5.

Solvent from the filtrate was evaporated under reduced pressure. Extracted the residue 6–7 times with 5 mL portions of carbon disulfide which on slow evaporation yielded a crop of pink colored crystals of dibenzoyl disulfide (1) Yield 72%. M.p. 134 °C (Lit. 134.5 °C). Anal. Calc. for $C_{14}H_{10}O_2S_2$: C, 61.29; H, 3.67. Found: C, 61.78; H, 3.36%.

2.2. Catalytic oxidation of thiophene-2-thiocarboxylic acid

The same procedure was applied as in case of thiobenzoaic acid. Reddish yellow crystals of 2,2'-thenoyl disulfide (**2**) were obtained. Yield 69%. M.p. 120 °C. *Anal.* Calc. for $C_{10}H_6O_2S_4$: C, 41.93; H, 2.11. Found: C, 41.78; H, 2.09%.



Scheme 1. Catalytic cycle for the oxidation of thiobenzoic acid.

2.3. Attempted oxidation of thiobenzoic acid using $AgNO_3(PPh_3)_2$ [synthesis of $Ag(SCOPh)(PPh_3)_2$ (**3**)]

To a solution of thiobenzoic acid (0.552 g, 4.0 mmol) in 10 mL methanol was added a methanolic solution (10 mL) of triethylamine (0.404 g, 4.0 mmol). After stirring for 30 min, 10 mL of the resulting solution was added dropwise to a magnetically stirred suspension of *bis*(triphenylphosphine)silver nitrate (0.347 g, 0.5 mmol) in ~15 mL methanol. After stirring the reaction mixture for 1 h the remaining portion of the triethylammonium thiobenzoate solution was slowly added into it. The reaction mixture was stirred overnight and yellow precipitate formed was filtered out. Recrystallized from chloroform. Yield 98%. M.p. 220 °C (dec). *Anal.* Calc. for C₄₃H₃₅O₁S₁P₂Ag: C, 67.11; H, 4.58. Found: C, 67.10; H, 4.58%.

2.4. Synthesis of Ag(SCOTh)(PPh₃)₂·2CHCl₃2H₂O (4)

To a suspension of $(PPh_3)_2AgNO_3$ (0.694 g, 1.00 mmol) in acetonitrile (10.0 ml), added a solution of sodium thiophene-2-thiocarboxylate (0.166 g, 1.00 mmol) in 5.0 ml of acetonitrile with stirring. After five minutes of addition an yellow precipitate was formed. The reaction mixture was stirred for an hour, collected the precipitate and dried under vacuum. The yellow powder was re-dissolved in chloroform, layered with petroleum ether (60–80 °C) then kept for crystallization. After two days yellow colored rod shape crystals suitable for single crystal X-ray diffraction were obtained. Yield: 92%. M.p. 208–210 °C. Anal. Calc. for $C_{43}H_{39}Cl_6O_3P_2S_2Ag: C, 49.17$; H 3.74. Found: C, 48.92; H, 3.71%. IR (KBr, cm⁻¹): 1566 ν (CO),



Scheme 2. Decomposition of silver thiobenzoate.



Fig. 1. Molecular structures of 1 and 2.

1183 v(C_{thiophene}-C), 1031 v(C-S). ¹H NMR (CDCl₃, δ ppm): 6.87–7.65 (Ph and Th ring).¹³C NMR 127.01–149.61 (Ph and Th ring), 195.81 (COS).

2.5. Synthesis of $[Ag_4(SCOTh)_4(PPh_3)_4]$ (5)

To a solution of PPh₃ (0.262 g, 1.00 mmol) in 10.0 mL methanol, added a solution of AgNO₃ (0.170 g, 1.00 mmol) in 5.0 mL of methanol, followed by a solution of sodium thiophene-2-thiocarboxylate (0.166 g, 1.00 mmol) in 5.0 ml of methanol with stirring. The reaction mixture was stirred for 2–3 h then dried under reduced pressure. The white residue was dissolved in toluene and filtered to remove NaCl. The filtrate was kept for crystallization. After

Table 2

Selected bond lengths and bond angles.

3 days colorless block shaped crystals were obtained. Yield: 0.420 (82%). M.p. 160–162 °C. *Anal.* Calc. for $C_{92}H_{72}O_4P_4S_8Ag_4$: C, 53.81; H, 3.53. Found: C, 53.54; H, 3.47%. IR (KBr, cm⁻¹): 1579 ν (CO), 1186 ν (C_{thiophene}-C), 1039 ν (C–S). ¹H NMR (CDCl₃, δ ppm): 6.88–7.70 (Ph and Th ring). ¹³C NMR: 127.04–148.10 (Ph and Th ring), 192.38 (COS).

2.6. X-ray crystallography

Single-crystal X-ray data for **1** and **3** were collected on Bruker SMART APEX CCD diffractometers while the same for **2**, **4** and **5** were collected on a Xcalibur Eos Oxford CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data integration and reduction for **1**, **3** and **2**, **4**, **5** were processed with SAINT and CRYSALISPRO softwares, respectively [12,13]. The structures were solved by the direct method and then refined on F^2 by the full-matrix least-squares technique with the SHELXL-97 software [14] using the WINGX (ver 1.70.01) program package [15]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were treated as riding atoms using SHELX default parameters. Other crystallographic data are summarized in Table 1.

3. Results and discussion

3.1. Oxidation of thiobenzoic acid

When excess thiobenzoic acid was treated with Ag(I) in presence of a base (triethylamine) dibenzoyldisulfide was obtained along with some other products described in the succeeding paragraph. The mechanism of this reaction (Scheme 1) is expected be analogous to that observed in the case of transition metal catalysed oxidation of thiols [16]. Two moles of thiobenzoate ions are oxidized to give one mole of dibenzoyl disulfide. One mole of water and half mole of dioxygen are consumed in each cycle. Oxygen involved in the reaction was not added but was obtained from air under ambient conditions. Bubbling oxygen gas in the reaction vessel did not improve the yield to any noticeable extent. However, the reaction when carried out under dry nitrogen atmosphere using anhydrous solvents did not yield the disulfide.

It is worth mentioning here that the reaction of Ag^+ ion with stoichiometric amount of sodium thiobenzoate in aqueous medium is reported to give Ag(SCOPh) complex in almost quantitative yields [17]. In our case also the catalytic oxidation of the thioacid is paralleled by a complex formation reaction where in a silver

Complex						
(A) Select	ed bond lengths					
1	S1-S2	2.0246(11)	S1-C8	1.833(3)	S2-C1	1.819(3)
	01-C8	1.203(3)	02-C1	1.212(3)	C1-C2	1.480(4)
2	S1-S3	2.0147(14)	S1-C1	1.810(4)	S3-C6	1.799(3)
	01-C1	1.200(4)	02-C6	1.204(4)	C1-C2	1.455(5)
4	Ag1–S1	2.515(3)	Ag1-01	2.919	Ag1–P1	2.477(2)
	Ag1-P2	2.462(2)	S1-C1	1.719(10)	01-C1	1.216(11)
5	Ag1–S1	2.5236(11)	Ag1–S3	2.5220(13)	Ag2–S1	2.5697(14)
	Ag2–S3	2.5096(11)	Ag1-P1	2.4234(13)	Ag2-P2	2.4016(9)
(B) Select	ed bond angles					
1	S2-S1-C8	100.17(9)	S1-S2-C1	101.38(9)	S2-C1-O2	121.4(2)
	S2-C1-C2	114.39(18)	02-C1-C2	124.2(2)	C1-C2-C3	117.7(2)
2	S3-S1-C1	100.95(12)	S1-S3-C6	102.24(12)	S1-C1-O1	121.9(3)
	S1-C1-C2	112.9(2)	01-C1-C2	125.2(3)		
4	S1-Ag1-P1	117.47(9)	S1-Ag1-P2	118.73(9)	P1-Ag1-P2	123.61(8)
5	S1-Ag1-S3	105.54(4)	S1-Ag1-P1	126.21(4)	S3-Ag1-P1	125.41(4)
	S3-Ag2-S1	93.47(4)	S3-Ag2-P2	139.30(4)	S1-Ag2-P2	126.72(4)
	Ag1-S1-Ag2	89.35(4)	Ag2-S3-Ag1	86.48(4)		



Fig. 2. Intermolecular interactions in 1.

complex, Ag(SCOPh) is formed. Interestingly, the complex Ag(SOCPh) is kinetically unstable and decomposes slowly in solution giving silver sulfide and dibenzoyl sulfide (Scheme 2). Similar decomposition has also been reported in some other cases [10].

Since the decomposition is due to the nucleophilic attack of the thiobenzoate ion on the carbonyl carbon of the Ag(SOCPh) complex, a higher concentration of the former in the reaction medium is expected to enhance the decomposition reaction. This was indeed observed when a reaction of AgNO₃ and PhOCSH was carried out in 1:10 M ratio. Ag₂S and (PhCO)₂S were obtained almost quantitatively and the excess thiobenzoate salt remained unreacted. Such a situation could be avoided by introducing the thiobenzoate salt very slowly and in batches.

In this proposed mechanism, when thiobenzoate anion is converted into the corresponding radical in presence of Ag⁺ ion the latter is reduced to the zero valent state. Metals in zero valent state play important role in many homogeneous catalytic processes. To stabilize such species (atomic) without allowing them to agglomerate into a metal lattice (solid) σ -donor/ π -acceptor ligands such as phosphines, carbonyl and dienes) are widely used. To increase the efficiency of the catalytic oxidation of the thiocarboxylate and if possible, to isolate a species containing silver in zero oxidation state we have carried out this reaction in presence of *bis*(triphenylphosphine)silver(I) nitrate. Surprisingly, no catalytic oxidation took place. Instead, the complex, [Ag(SCOR)(PPh_3)_2] (R = Ph or Th) were isolated in good yields. Attempts to carryout the catalytic oxidation under lower concentration of substrate also led to the formation of a stable complex [Ag(SCOR)(PPh_3)]_4.

3.2. Crystal and molecular structures

The products of the catalytic reactions, dibenzoyl disulfide and 2,2'-dithenoyl disulfide were characterized crystallographically. The unit cells in both the cases are monoclinic with $P2_1/c$ space group. Molecular structures of **1** and **2** are given in Fig. 1 and

selected bond lengths and angles are listed in Table 2. The Ph-COS units are as expected, almost planar, however, the two units are almost perpendicular to each other the CSSC torsional angles being 80.6° and 86.3° in **1** and **2**, respectively. As a result the two carbonyl oxygens are quite away from each other. One may expect existence of intramolecular hydrogen bonds due to the close placing of atoms, CH···O (2.570 Å in **1**) and CH···S (2.632 Å in **1** and 2.786 Å in **2**), however, the C–H–Y (Y = O/S) angles are too small (varying between 97.95° and 108.98°) to allow such bonding [18]. Intermolecular CH···O bonds are, however, present as shown in both the cases. The molecules pack in such a way that channel like structures are formed in the lattice. In the case of **1** a distance of **3**.8 Å between the centroids of two adjacent parallel phenyl



Fig. 3. Molecular structure of 4 (hydrogen are omitted for clarity).



Scheme 3. Possible bonding modes of thiophene-2-thiocarboxylate ligand.



Fig. 4. Molecular structure of 5 (hydrogen and phenyl ring carbon atoms are omitted for clarity).

rings (as shown by the thin solid line in Fig. 2) indicates the existence of strong intermolecular π - π interactions.

Synthesis and structure of **3** have already been reported by Vittal et al. [19]. The molecule crystallizes in a triclinic system with $P\bar{1}$ space group (Table 2). Though we could refine the structure much better than that reported earlier there is no point in discussing the structural details further.

Complex **4** crystallized in monoclinic system with space group $P2_1/n$. Molecular structure is depicted in Fig. 3 and selected bond length and bond angles are given in Table 1.

Two molecules of each water and chloroform were crystallized with each molecule of **4** in which one chloroform molecule is disordered. The molecular structure is similar to that of **3**; the silver atom is bonded to two phosphorus atoms of triphenylphosphine and one sulfur atom of thiophene-2-thiocarboxylate group. Though the ligand possesses three possible donor sites and may exhibit quite a few different bonding modes (Scheme 3) only S1, the sulfur of the thiocarboxylate group coordinates to the metal.

The Ag–O1 distance (2.910 Å) is quite longer than the sum of the covalent radii of the two atoms (2.13 Å) and any significant interaction between the two atoms is unlikely. The geometry around Ag atom is trigonal planar and it lies in the plane constituted by S_1 , P_1 and P_2 atoms.

Complex **5** have an eight member ring constituted by the four silver and four sulfur atoms arranged alternately in a chair conformation (Fig. 4). Selected bond lengths and bond angles are given in Table 1. Four silver atoms and four sulfur atoms of thiocarboxylate constitute an eight membered ring with a crystallographic inversion centre at the middle. Each silver atom is bonded to one phosphorus atom of triphenyl phosphine and two sulfur atoms of two thiocarboxylate ligands. Silver atom is tipped above the plane constituted by P, S and S plane atoms by 0.757 Å. Though the structure

is analogous to those of $[Ag(SCOPh)(PPh_3)]_4 \cdot 2CH_2Cl_2$ and $[Ag(S-COPh)(PPh_3)]_4 \cdot C_6H_5CH_3$ reported by Vittal et al. [15], there are significant differences as well.

Ag–S–Ag–S dihedral angles are 5.37° and 7.86° while S–Ag–S–Ag are 165.81° and 131.86° respectively in **5** and [Ag(SCOPh)(PPh₃)]₄·2CH₂Cl₂. The Ag₄S₄ ring in **5** is more puckered as compared to that of [Ag(SCOPh)(PPh₃)]₄·2CH₂Cl₂. The Ag2–Ag2′ distance across the chair in the former is much shorter (3.657 Å) than the latter (4.458 Å). Similarly, the Ag–S distances across the chair (3.182 Å) are significantly shorter than those in the reported structure (4.519 Å). The most significant difference in the structure is the arrangement of thiocarboxyl groups. The O atoms (O2 and O2′) in **5** face away from the eight membered ring as opposed to the observed orientation in the corresponding thiobenzoate complexes in which the O atoms are placed above and below the ring. It may be mentioned here that both solvent and substitution on thiocarboxylate groups are known to influence the solid state structures of the eight membered rings.

Acknowledgement

Financial support to S.B. and fellowships to S.S. and J.C. from the Council of Scientific and Industrial Research, New Delhi, are gratefully acknowledged.

Appendix A. Supplementary data

CCDC 705265, 780187, 780188, 780189 and 780190 contains the supplementary crystallographic data for compounds **1**, **2**, **3**, **5** and **4**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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