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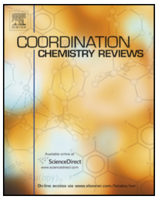

Review

Coordination chemistry of the thiosalicylate ligand

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Contents

Abbreviations: bipy, 2,2′-bipyridine; cod, cycloocta-1,5-diene; Cp, η^5–cyclopentadienyl; Cy, cyclohexyl; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; ESI (MS), Electrospray ionisation (mass spectrometry); H_2tsal, thiosalicylic acid; phen, 1,10-phenanthroline; PPN$^+$, bis(triphenylphosphine)iminium, $(Ph_3P)_2N^+$; py, pyridine; thf, tetrahydrofuran.

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ABSTRACT

Thiosalicylic acid (2-mercaptobenzoic acid, o-$HSC_6H_4CO_2H$) is an interesting hybrid hard-soft donor ligand, able to coordinate a very wide range of metal centres from the entire periodic table, as either a mono- or di-anion, with a wide range of coordination modes, from simple monodentate through to various bridging modes. This review article summarises the coordination chemistry of the thiosalicylate ligand, with an emphasis on recent developments, especially where X-ray crystallography has been used to provide unequivocal evidence of the binding mode(s) of the thiosalicylate ligand. Applications of the thiosalicylate ligand in materials chemistry are also summarised.

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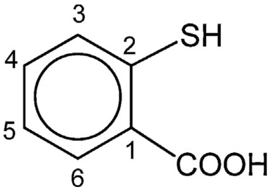
1. Introduction

Thiosalicylic acid (2-mercaptobenzoic acid, o-$HSC_6H_4CO_2H$) **1** is able to coordinate (typically as a deprotonated ligand) to a very wide range of metal centres from the entire periodic table. This is accomplished by the presence of both hard (carboxylate) and soft (thiolate) donors. While the coordination chemistry of thiosalicylate ligand has a long history, this review focuses on more recent developments, and systems that have been fully characterised, particularly where there is X-ray structural characterisation. Applications of thiosalicylate ligands are also briefly reviewed. Related thioethers (RSC_6H_4COOH) and carboxylate esters (HSC_6H_4COOR) also form effective ligands, but are not included in this review because of space restrictions. Likewise, the nitrogen-substituted derivative 2-mercaptonicotinic acid, as well as the 3- and 4- isomers of mercaptobenzoic acid also show extensive coordination chemistries, but space also precludes a discussion of these systems [1].

2. Thiosalicylic acid and the thiosalicylate ligand

Thiosalicylic acid **1** (Scheme 1) is a hybrid thiol-carboxylic acid, often known by alternative names such as 2-mercaptobenzoic acid, *ortho*-mercaptobenzoic acid, or alternatively 2-sulfanylbenzoic acid. It is readily commercially available as an odourless, off-white solid which is readily soluble in lower alcohols, poorly soluble in water at acidic pH, but readily soluble under alkaline conditions. The compound is a diprotic acid with pK_a values of 4.92 and 9.96 for the first and second proton dissociations respectively [2]. In a more recent study, pK_{a1} and pK_{a2} values of 3.76 ± 0.05 and 8.33 ± 0.07 were reported [3]. ^1H and $^{13}C\{^1H\}$ NMR spectra of thiosalicylic acid have been reported [4], and are shown in Tables 1 and 2, respectively; the atom numbering scheme is shown in Scheme 1.

In the solid state, thiosalicylic acid is stable to air, making it a conveniently handled ligand. However, similar to other thiols, it is fairly easily oxidised to its disulfide, Scheme 2; these processes have been investigated using electrochemistry [5]. In a recent study, the formation of $HOOCC_6H_4SSC_6H_4COOH$ from thiosalicylic acid under hydrothermal conditions was investigated with variation of the pH. In acidic conditions, thiosalicylic acid remained unchanged, but on increasing the pH, 50% oxidation



Scheme 1. The atom numbering scheme of thiosalicylic acid **1**.

Table 1
^1H NMR chemical shifts and coupling constants (*J*) for thiosalicylic acid in $CDCl_3$ and $(CD_3)_2SO$ [s = sharp, br = broad], from ref [4]; refer to Scheme 1 for the atom numbering scheme.

	Solvent	
	$CDCl_3$	$(CD_3)_2SO$
H3	7.31 dd (J 7.1, 1.2)	7.49 dd (J 8.1, 0.9)
H4	7.35 ddd (J 7.5, 7.5, 1.4)	7.35 ddd (7.8, 7.8, 1.7)
H5	7.10 ddd (J 7.5, 7.5, 1.2)	7.16 ddd (J 7.5, 7.5, 1.1)
H6	8.12 dd (J 7.8, 1.8)	7.91 dd (J 8.0, 1.4)
OH	Unobserved	13.01 br
SH	4.61 s	5.33 br

Table 2
$^{13}C\{^1H\}$ NMR chemical shifts for thiosalicylic acid in $CDCl_3$ and $(CD_3)_2SO$ from Ref [4]; refer to Scheme 1 for the atom numbering scheme.

	Solvent	
	$CDCl_3$	$(CD_3)_2SO$
C1	124.8	126.5
C2	139.3	138.1
C3	131.1	130.9
C4	133.3	132.4
C5	124.8	124.6
C6	132.7	131.4
C=O	171.5	167.6

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