Citation for published version (APA):
Formation of ortho-cyano-aminothiophenolate ligands with versatile binding modes via facile carbon-sulfur bond cleavage of 2-aminobenzothiazoles at mercury(II) centres#

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Addition of 2-aminobenzothiazole and substituted derivatives to mercuric acetate in warm ethanol leads to the high yield formation of $[\text{Hg}\{\text{SC}_6\text{H}_2\text{XN} \text{(C≡N)}\}]_n$ resulting from loss of hydrogen and sulfur-carbon bond cleavage. Addition of phosphines affords a series of complexes in which the new ortho-cyano-aminothiophenolate ligands adopt three different binding modes.

The coordination chemistry of ortho-aminothiophenolate ligands has been extensively studied 1-8 as they have been shown to be non-innocent being capable of varying their oxidation and protonation levels. The vast majority of such chemistry focuses on the parent ligand as it is easily accessible from ortho-aminothiophenol or ortho-aminophenyl disulfide. In contrast N-functionalised derivatives do not appear to have previously been reported despite such analogues allowing for the fine-tuning of both steric and electron properties. A particularly rare amino-stubstituent is the cyano group, 9-10 yet such species could potentially exhibit interesting electronic properties resulting from the potential delocalisation of electron-density over the N-C≡N moiety. Herein we report the facile serendipitous generation of such species at a mercury(II) centre upon simple addition of 2-aminobenzothiazole and related 5-substituted derivatives.

In warm ethanol, addition of 2-aminobenzothiazole and mercuric acetate leads to the rapid formation of a yellow precipitate in high yields (Scheme 1), a similar observation being noted with 2-amino-5-X-benzothiazoles (X = Cl, Br). Based on analytical and spectroscopic data these species are believed to have the formula $[\text{Hg}\{\text{SC}_6\text{H}_2\text{XN} \text{(C≡N)}\}]_n$ (1a-c) the value of n being unknown. Their most noteworthy spectroscopic feature is the unexpected observation of a strong absorption between 2140-2125 cm\(^{-1}\) associated with a cyanide group. Such complexes result from the double deprotonation of the 2-aminobenzothiazoles and insertion of mercury(II) into a carbon-sulfur bond.

![Scheme 1. Reaction of 2-aminothiazoles with mercuric acetate](image)

We have not been able to crystallographically characterise these species and are consequently unable to unambiguously assign the ligand coordination mode. They do, however, react readily with a range of phosphines at room temperature to form adducts, four of which we have crystallographically characterised, namely $[\text{Hg}\{\text{SC}_6\text{H}_2\text{XN} \text{(C≡N)}\} \text{(PPh}_3\text{)}]\_n$ (2), $[\text{Hg}\{\text{SC}_6\text{H}_2\text{CIN} \text{(C≡N)}\} \text{(PPh}_3\text{)}]\_n$ (3), $[\text{Hg}\{\text{SC}_6\text{H}_2\text{BrN} \text{(C≡N)}\} \text{(PPh}_3\text{)}]\_n$ (4), $[\text{Hg}\{\text{SC}_6\text{H}_2\text{N} \text{(C≡N)}\} \text{(PPh}_3\text{)}]\_n$ (5). In these complexes the ortho-cyano-aminothiophenolate ligand displays three different coordination modes (A-C) (Chart 1).

![Chart. Different binding modes of ortho-cyano-aminothiophenolate ligands](image)

Reaction of bis(diphenylphosphino)ethane (dppe) with 1a proceeds at room temperature over 1 h, the yellow precipitate slowly dissolving to afford a clear yellow solution. The molecular structure of $[\text{Hg}\{\text{SC}_6\text{H}_2\text{N} \text{(C≡N)}\} \text{(PPh}_3\text{)}]\_n$ (2) is shown in Figure 1. The complex is a one-dimensional coordination polymer consisting of tetrahedral mercury(II) centres linked by the diphenylphosphines. Most notably the ortho-cyano-aminothiophenolate ligand binds in a simple chelating fashion (A Chart 1) subtending and angle of 81.3(3)° at mercury. Both mercury-sulfur and mercury-nitrogen bond lengths of 2.530(4) and 2.300(11) Å are within the expected ranges. This binding mode is akin to that previously found for mercury(II) 1.2-benzenediithiolate complexes such as $[\text{Hg}\{\text{SC}_6\text{H}_2\text{S}_2\}]_n [\text{NEt}_3\text{]}_2$ 11. Crystallographic data for 2 is only of moderate quality and we were only able to refine the carbon of the NCN unit isotropically. Consequently it is not appropriate to discuss the precise bond lengths within the ligand but that the C≡N subunit is maintained is clearly seen by the observation of a
strong resonance at 2138 cm\(^{-1}\) in the IR spectrum. The structure of 2 is akin to that of [Hg(SC\(_5\)S\(_5\))(Ph\(_3\)PCH\(_2\))]\(_n\) reported by McKenzie and co-workers in which the dithiolate ligand subtends an angle of 89.56(8)\(^\circ\) at the metal centre and mercury-sulfur bonds are 2.560(3) and 2.530(3) Å\(^{12}\).

Addition of triphenylphosphine to 1b-c resulted in the isolation of [Hg\{(SC\(_6\)H\(_4\)N(C≡N))\}(PPh\(_3\))]\(_2\) (3) and [Hg\{(SC\(_6\)H\(_4\)BrN(C≡N))\}(PPh\(_3\))]\(_2\) (4) respectively as pale yellow solids. The two are isostructural and consequently only the results of 4 will be discussed, the molecular structure of which is displayed in Figure 2. The molecule is dimeric and consists of a central Hg-S\(_2\) core with each mercury centre also being coordinated to one phosphine and a nitrogen of an N=C=N moiety. Thus, the ortho-cyano-aminophenolate ligand binds in mode B (Chart 1). Both the mercury-sulfur and mercury nitrogen bond lengths are somewhat shorter than those found in 2 and the mercury-phosphorus distance is longer. Most importantly the better quality structural data allows the unambiguous confirmation of the N=C=N subunit which is linear [N1-C1-N2 1.287(8) Å] and consists of long [N1-C1 1.154(8) Å] and short [N2-C1 1.154(8) Å] nitrogen-carbon bonds.

Addition of triphenylphosphine to 1a-c proceeded in an analogous fashion to that observed for 1b-c and small yellow crystals of [Hg(SC\(_6\)H\(_4\)N(C≡N))\](PPh\(_3\))]\(_2\) (5) were readily grown. An X-ray crystallographic study, however, yielded a quite unexpected result as illustrated in Figure 3 which shows the molecular structure of 5. Like both 3 and 4, the molecule is a centrosymmetric dimer but now it is the cyano groups that link together the two monomeric units (C in Chart 1). This results in formation of an eight-membered Hg\(_3\)N\(_3\)C\(_2\) ring which because of the linear nature of the N=C=N subunit is akin to a chair configuration of a six-membered ring. The bite-angle of the ortho-cyano-aminophenolate ligand of 81.76(11)\(^\circ\) differs little from those found in 2-4 suggesting that the different bonding modes observed are similar in energy. As expected, the two mercury-nitrogen distances differ significantly the longer Hg1-N2A length of 2.517(5) Å being akin to a simple mercury-amine interaction. Perhaps most importantly, adoption of this bonding mode has little effect on the redox active ligands in catalysis and materials chemistry.

The mode of formation of 1a-c is still under investigation. The reaction appears to be unique to mercuric acetate since with other mercury salts simple 2-aminobenzothiazole adducts result.\(^{13,14}\) Related to the work presented here are examples of the metal-mediated ring opening of benzothiazoles which has been utilised to prepare Schiff-base chelates,\(^{15}\) while it is also noteworthy that 2-aminobenzothiazole complexes of mercury(II) have been known for over a century\(^{16}\) being developed as the basis of a gravimetric determination of mercury(II) at the milligram level.\(^{17}\) Thus it appears that the transformation of 2-aminobenzothiazoles into ortho-cyano-aminophenolate ligands has been awaiting discovery for some time. The facile nature of this process allows us a unique access to ortho-cyano-aminophenolate ligand and we are currently investigating transmetalation reactions as a means to accessing this ligand on other metal centres and also applications of this class of redox-active ligands in catalysis and materials chemistry.
We are grateful to the Commonwealth Scholarship Commission for the award of a Commonwealth Scholarship to S.G. and the Erasmus Mundus programme for a postdoctoral scholarship to S.B.-M. We thank Dr Nathan Hollingsworth for help with aspects of this work and Professor S.A. Al-Jibori thanks the University of Tikrit for financial support.

Notes and references


