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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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10 Addition of 2-aminobenzothiazole and substituted derivatives to
mercuric acetate in warm ethanol leads to the high yield
formation of $[\text{Hg}\{\text{SC}_6\text{H}_3\text{XN}(\text{C}\equiv\text{N})\}]_n$ resulting from loss of
hydrogen and sulfur-carbon bond cleavage. Addition of
phosphines affords a series of complexes in which the new *ortho*-
15 cyano-aminothiophenolate ligands adopt three different binding
modes.

The coordination chemistry of *ortho*-aminothiophenolate ligands has
been extensively studied¹⁻⁸ as they have been shown to be non-
innocent being capable of varying their oxidation and protonation
20 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
25 electron properties. A particularly rare amino-substituent 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
30 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
35 noted with 2-amino-5-X-benzothiazoles (X = Cl, Br). Based on
analytical and spectroscopic data these species are believed to
have the formula $[\text{Hg}\{\text{SC}_6\text{H}_3\text{XN}(\text{C}\equiv\text{N})\}]_n$ (**1a-c**) the value of n
being unknown. Their most noteworthy spectroscopic feature is
the unexpected observation of a strong absorption between 2140-
40 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.

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[#] Electronic supplementary information (ESI) available: Experimental details, characterising data, ORTEP figures, for all complexes

Scheme 1. Reaction of 2-aminobenzothiazoles with mercuric acetate

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
55 readily with a range of phosphines at room temperature to form
adducts, four of which we have crystallographically
characterised, namely $[\text{Hg}\{\text{SC}_6\text{H}_4\text{N}(\text{C}\equiv\text{N})\}(\text{PPh}_3)_2]_n$ (**2**),
 $[\text{Hg}\{\text{SC}_6\text{H}_3\text{ClN}(\text{C}\equiv\text{N})\}(\text{PPh}_3)_2]$ (**3**),
 $[\text{Hg}\{\text{SC}_6\text{H}_3\text{BrN}(\text{C}\equiv\text{N})\}(\text{PPh}_3)_2]$ (**4**), $[\text{Hg}\{\text{SC}_6\text{H}_4\text{N}(\text{C}\equiv\text{N})\}(\text{PPh}_3)_2]$
60 (**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

Reaction of bis(diphenylphosphino)ethane (dppe) with **1a**
65 proceeds at room temperature over 1 h, the yellow precipitate
slowly dissolving to afford a clear yellow solution. The molecular
structure of $[\text{Hg}\{\text{SC}_6\text{H}_4\text{N}(\text{C}\equiv\text{N})\}(\text{PPh}_2\text{PCH}_2)_2]_n$ (**2**) is shown in
Figure 1. The complex is a one-dimensional coordination
polymer consisting of tetrahedral mercury(II) centres linked by
70 the diphosphine ligands. Most notably the *ortho*-cyano-
aminothiophenolate ligand binds in a simple chelating fashion (**A**
Chart 1) subtending an 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
75 previously found for mercury(II) 1,2-benzenedithiolate complexes
such as $[\text{Hg}(\text{SC}_6\text{H}_4\text{S})_2][\text{NEt}_4]_2$.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
80 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(SC₃S₃)(Ph₂PCH₂)₂]_n reported by McKenzie and co-workers in which the dithiolate ligand subtends an angle of 89.56(8)° at the metal centre and mercury-sulfur bonds are 2.560(3) and 2.530(3) Å.¹²

Fig. 1. Molecular structure of the repeating unit of **2**. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths [Å] and bond angles [deg]: Hg-N1 2.300(11), Hg-S1 2.530(4), Hg-P1 2.486(3), Hg-P2 2.494(3); S1-Hg-N1 81.3(3), P1-Hg-P2 129.45(9).

Addition of triphenylphosphine to **1b-c** resulted in the isolation of [Hg{SC₆H₃CIN(C≡N)}(PPh₃)₂] (3) and [Hg{SC₆H₃BrN(C≡N)}(PPh₃)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 Hg₂S₂ core with each mercury centre also being coordinated to one phosphine and a nitrogen of an N-C≡N moiety. Thus, the *ortho*-cyano-aminothiophenolate 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 174.6(7)°] and consists of long [N1-C1 1.287(8) Å] and short [N2-C1 1.154(8) Å] nitrogen-carbon bonds.

Fig. 2. Molecular structure of **4**. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths [Å] and bond angles [deg]: Hg1-N1 2.266(5), Hg1-S1 2.411(2), Hg1-S1A 2.871(2), Hg1-P1 2.272(2), N1-C1 1.287(8), N2-C1 1.154(8); Hg1-S1-Hg1A 83.57(5), S1-Hg1-S1A 96.43(5), S1-Hg1-N1 80.76(14), P1-Hg-S1 151.40(6), P1-Hg1-N1 122.19(13), N1-C1-N2 174.6(7).

Addition of triphenylphosphine to **1a** proceeded in an analogous fashion to that observed for **1b-c** and small yellow crystals of [Hg{SC₆H₄N(C≡N)}(PPh₃)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 Hg₂N₄C₂ 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-aminothiophenolate ligand of 81.76(11)° 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 bond distances within the N-C≡N moiety, which still displays long and short interactions [N1-C1 1.287(6), N2-C1 1.153(6) Å]. This is also reflected in the observation of a strong C≡N stretch at 2140 cm⁻¹ in the IR spectrum.

Fig. 3. Molecular structure of **5**. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths [Å] and bond angles [deg]: Hg1-N1 2.312(4), Hg1-S1 2.352(2), Hg1-P1 2.373(2), Hg1-N2A 2.517(5), N1-C1 1.287(6), N2-C1 1.153(6), S1-Hg1-N1 81.76(11), N1-Hg1-N2A 91.86(14), S1-Hg1-P1 147.76(5), N1-Hg1-P1 122.04(11), N1-C1-N2 176.2(6).

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 century¹⁶ 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-aminothiophenolate ligands has been awaiting discovery for some time. The facile nature of this process allows us a unique access to *ortho*-cyano-aminothiophenolate 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.

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