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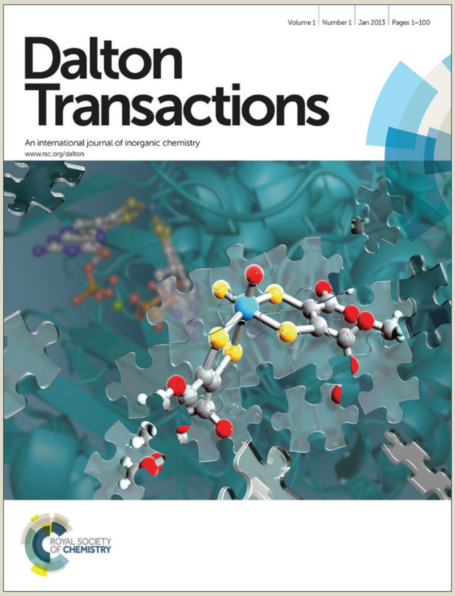

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Formation of *ortho*-cyano-aminothiophenolate ligands with versatile binding modes *via* facile carbon-sulfur bond cleavage of 2-aminobenzothiazoles at mercury(II) centres[#]

Subhi A. Al-Jibori,[*a] Ahmed A. Irzoqi,[b] Emad G.H. Al-Saraj,[a] Ahmed S.M. Al-Janabi,[c] Sucharita Basak-Modi,[d] Shishir Ghosh[d], Kurt Merzweiler[e], Christoph Wagner[e], Harry Schmidt[e] and Graeme Hogarth,[*f]

***Receipt/Acceptance Data* [DO NOT ALTER/DELETE THIS TEXT]**
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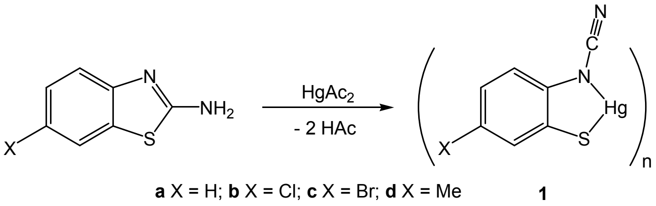
DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

Addition of 2-aminobenzothiazole and substituted derivatives to mercuric acetate in warm ethanol leads to the high yield formation of [Hg{$SC_6H_3XN(C{\equiv}N)$}]$_n$ 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 bis(*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 electronic 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 upon simple addition of 2-aminobenzothiazole and related 5-substituted derivatives.

In warm ethanol, addition of 2-aminobenzothiazole to 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, Me). Based on analytical and spectroscopic data these species are believed to have the formula [Hg{$SC_6H_3XN(C{\equiv}N)$}]$_n$ (**1a-d**), 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

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, three of which we have crystallographically characterised; [Hg{$SC_6H_3MeN(C{\equiv}N)$}{$Ph_2P(CH_2)_4PPh_2$}]$_n$ (**2**) [Hg{$SC_6H_3BrN(C{\equiv}N)$}(PPh_3)]$_2$ (**3**), [Hg{$SC_6H_4N(C{\equiv}N)$}(PPh_3)]$_2$ (**4**). In these complexes the *ortho*-cyano-aminothiophenolate ligand displays three different coordination modes (**A-C**) (Chart 1).

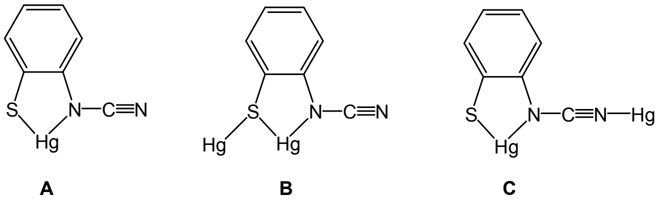


Chart. Different binding modes of *ortho*-cyano aminothiophenolate ligands

Reaction of bis(diphenylphosphino)butane (dppb) with **1d** proceeds at room temperature over 1 h, the yellow precipitate slowly dissolving to afford a clear yellow solution. The molecular structure of [Hg{$SC_6H_3MeN(C{\equiv}N)$}{$Ph_2P(CH_2)_4PPh_2$}]$_n$ (**2**) is shown in Figure 1. The complex is a one-dimensional coordination polymer consisting of tetrahedral mercury(II) centres linked by the diphosphine ligands. Most notably the *ortho*-cyano-aminothiophenolate ligand binds in a simple chelating fashion (**A** Chart 1) subtending and angle of 81.13(9)° at mercury. Both mercury-sulfur and mercury-nitrogen bond lengths of 2.437(1)

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[a] *Department of Chemistry, College of Science, University of Tikrit, Tikrit, Iraq. E-mail: subhi_aljibori@yahoo.com*
[b] *Department of Chemistry, College of Education, University of Tikrit, Tikrit, Iraq.*
[c] *Department of Chemistry, College of Veterinary Medicine, University of Tikrit, Tikrit, Iraq.*
[d] *Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK.*
[e] *Institut für Chemie, Martin-Luther-Universität, Halle-Wittenberg, Kurt-Mothes-Str.2, D-06120 Halle, Germany.*
[f] *Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London, SE1 1DB, UK. E-mail: graeme.hogarth@kcl.ac.uk*
[#] Electronic supplementary information (ESI) available: Experimental details, characterising data, ORTEP figures, for all complexes

and 2.275(3) Å are within the expected ranges. This binding mode is akin to that previously found for mercury(II) 1,2-benzenedithiolate complexes such as $[Hg(SC_6H_4S)_2][NEt_4]_2$.[11] That the C≡N subunit is maintained upon addition of the diphosphine is clearly seen by the observation of a strong absorption at 2138 cm^{-1} in the IR spectrum. This is in accord with the linear nature of the N-C≡N moiety [N1-C7-N2 177.45(5)°] and the significant difference in the nitrogen-carbon bonds [N1-C7 1.307(5), N2-C7 1.149(6) Å]. The structure of **2** is akin to that of $[Hg(SC_3S_3S)(Ph_2PCH_2CH_2PPh_2)]_n$ 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]

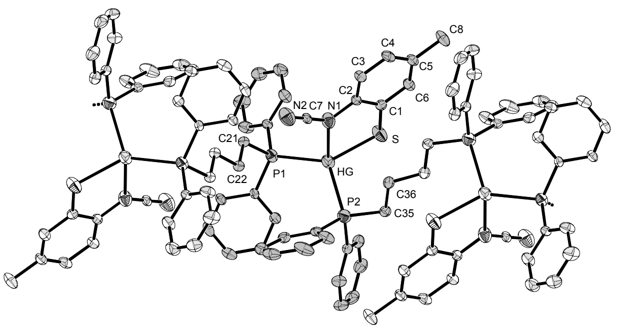

Fig. 1. Molecular structure of the repeating units of **2**. Selected bond lengths [Å] and bond angles [deg]: Hg-N1 2.275(3), Hg-S 2.4369(9), Hg-P 2.3918(9), N1-C7 1.307(5), N2-C7 1.149(6); S-Hg-N1 81.13(9), N1-C7-N2 177.4(5).

Addition of triphenylphosphine to **1c** resulted in the isolation of $[Hg\{SC_6H_3BrN(C≡N)\}(PPh_3)]_2$ (**3**) as a pale yellow solid (Figure 2). The molecule is dimeric and consists of a central Hg_2S_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-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.

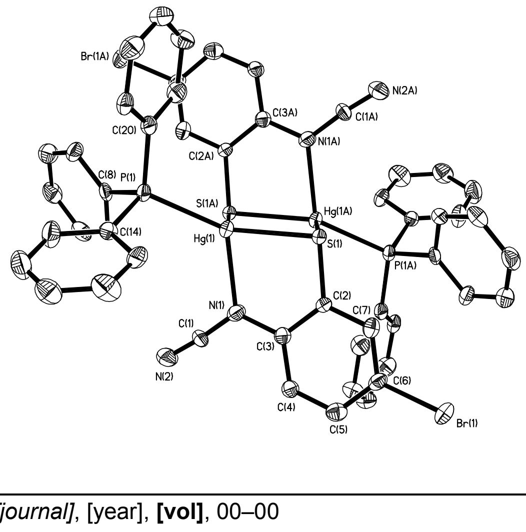

Fig 2. Molecular structure of **3**. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths [Å] and bond angles [deg]: Hg1-N1 2.266(5), Hg1-S1 2.411(2), Hg1-S1A 2.871(2), Hg1-P1 2.272(2), N1-C1 1.287(8), N2-C1 1.154(8); Hg1-S1-Hg1A 83.57(5), S1-Hg1-S1A 96.43(5), S1-Hg1-N1 80.76(14), 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 **1c** and small yellow crystals of $[Hg\{SC_6H_4N(C≡N)\}(PPh_3)]_2$ (**4**) 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 **4**. Like **3**, 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 $Hg_2N_4C_2$ 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-aminothiophenolate ligand of 81.76(11)° differs little from those in **2-3** 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.

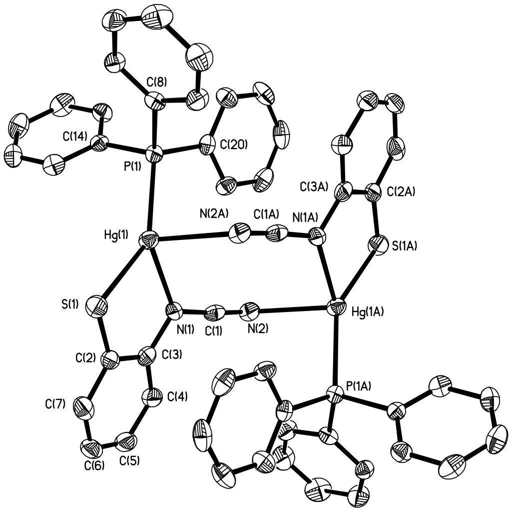

Fig. 3. Molecular structure of **4**. Thermal ellipsoids are displayed at 50% probability. Selected bond lengths [Å] and bond angles [deg]: Hg1-N1 2.312(4), Hg1-S1 2.352(2), Hg1-P1 2.373(2), Hg1-N2A 2.517(5), N1-C1 1.287(6), N2-C1 1.153(6), S1-Hg1-N1 81.76(11), N1-Hg1-N2A 91.86(14), S1-Hg1-P1 147.76(5),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

The mode of formation of **1a-d** 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] While transition-metal mediated carbon-sulfur bond activation is quite common[15] examples involving mercury are rare[16]. 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,[17] while it is also noteworthy that 2-aminobenzothiazole complexes of mercury(II) have been known for over a century,[18] being developed as the basis of a gravimetric determination of mercury(II) at the milligram level.[19] 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.

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. Professor S.A. Al-Jibori thanks the University of Tikrit for financial support.

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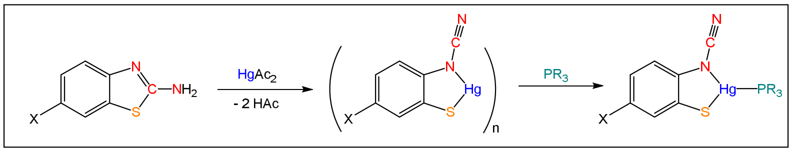

Reactions of 2-aminobenzothiazoles with mercuric acetate leads to the high yield formation of coordination polymers $[Hg\{SC_6H_3XN(C\equiv N)\}]_n$ resulting from loss of hydrogen and sulfur-carbon bond cleavage, addition of phosphines affording soluble adducts in which the *ortho*-cyano-aminothiophenolate ligands adopt three different binding modes.