Reactivity of Hg(II) ortho-cyano-aminothiophenolate coordination polymers [Hg{SC₆H₄X(N(C≡N))}ₙ] with cyclic aromatic amines, Ph₃P = E (E = O, S) and [HgCl₂(k²-phen)]

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ABSTRACT

We report reactions of Hg(II) ortho-cyano-aminothiophenolate coordination polymers, [Hg{SC₆H₄X(N(C≡N))}ₙ] with donor ligands. Addition of cyclic aromatic amines, such as pyridine (L), leads to breakdown of the polymeric structure to give mononuclear four-coordinate complexes, [Hg{2,2'-bipy}L₂], while 2,2'-bipy and 1,10-phen (L₂) similarly afford mononuclear chelate complexes [Hg{2-SC₆H₄X(N(C≡N))}k²-L₂]. In contrast, Ph₃P = E (E = O, S) form 1:1 complexes which, on the basis of related phosphine adducts, are formulated as binuclear [Hg{μ-SC₆H₄X(N(C≡N))}k²-E = PPh₃]. Reaction of [Hg{SC₆H₄N(C≡N)}ₙ] with [HgCl₂(k²-phen)] affords an adduct tentatively formulated as [Hg{2-SC₆H₄X(N(C≡N))}(μ-Cl)₂Hg(k²-phen)] in which the two chlorides bridge the Hg-Hg vector.

1. Introduction

Extended inorganic systems [1], as exemplified by 3D metal-organic frameworks (MOFs) [2, 3], have become an area of intense research over the past 25+ years having a wide range of potential applications [4]. The simplest such systems are 1D coordination polymers which are known for a wide range of metals [5] but are especially prevalent for Hg(II) [6]. We recently reported the synthesis of a small series of Hg(II) coordination polymers, [Hg{SC₆H₄X(N(C≡N))}ₙ] (X = H, Me, Cl, NO₂, Br) (1a-e),

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containing the redox active ortho-cyano-aminothiophenolate (ocap) ligand, resulting from dehydrogenation and C-S bond cleavage of 2-aminobenzothiazoles upon reaction with Hg(OAc)₂ [7, 8]. While we were unable to crystallographically characterize any examples of these complexes, the dehydrogenative ring-scission was unambiguously confirmed from reactions with a range of mono- and bidentate phosphines, which afforded a series of crystallographically characterized species [7, 8]. An unexpected feature of the latter was the range of coordination modes the ocap ligand adopts, with four distinct binding modes being seen in the solid-state (Chart 1). Thus, the ring sulfur, nitrogen and also the cyanide nitrogen are able to bind to the Hg(II) center, and in 1a-e it is believed that all three are bound thus enabling a polymeric network to be established [7, 8]. In reactions with phosphines, while this network is disrupted, we were surprised to find that monodentate complexes [Hg(κ²-ocap)(PR₃)₂], in which the ocap ligand acts as a simple bidentate (A), were only formed upon addition of either excess of PPh₃ or the chelating diphosphine, 1,1'-bis(diphenylphosphino)ferrocene (dppf) [8]. Indeed, [Hg(κ²-ocap)(PPh₃)₂] are not very stable and readily lose phosphine to afford dimeric complexes with bridging ocap ligands [8].

In further developing this interesting class of redox-active ligands [9], we have taken two approaches. The first is to transmetallate the ocap ligand onto a variety of transition metals in order to enhance the redox interactions between the two [10], and the second is to expand the range of two-electron donor ligands to push the system towards adoption of simple chelate binding (Scheme 1). Herein, we develop this latter approach, focusing on reactions of a range of N-donor cyclic aromatic amines and also O and S donor ligands in the form of Ph₃P = E (E = O, S).

2. Results and discussion

2.1. Reactions with 2-electron N-donor ligands

Pyridine (py) is known to react with simple Hg(II) salts to afford adducts, for example with HgBr₂ or HgI₂ tetrahedral mononuclear complexes [HgX₂(py)₂] [11, 12], although

![Chart 1. Binding modes (A-D) of the ortho-cyano-aminothiophenolate (ocap) ligand adopted in phosphine complexes.](image)

![Scheme 1. Target mononuclear ocap complexes from reactions of 1 with 2-electron donor ligands (L).](image)
such chemistry is not always so simple. Thus with HgCl₂, addition of pyridine leads to
formation of a coordination polymer in which chlorides bridge six-coordinate Hg(II)
centers [11]. Addition of two equivalents of pyridine to 1 b-c in CHCl₃ resulted in for-
mation of [Hg(SC₆H₃XN(C≡N))(py)₂] (2 b-c) in good yields. For 2 b, integration of the
methyl resonance against signals in the aromatic region showed a ratio of pyridine to
ocap of 2:1, and this was supported by the elemental analysis. While this does not
unequivocally rule out the possibility of dimeric or polymeric structures, we strongly
favor formation of mononuclear species (Scheme 2). With pyrazole (pz), related com-
plexes [Hg(SC₆H₃XN(C≡N))(pz)₂] (3 b-c) were similarly formed. We next turned our
attention to reactions with 2-aminopyridine (2-ampy) and 2-aminopyrimidine (2-
ampym), both of which have the potential to bind through either the ring nitrogen or
the amine group. Complexes 4 b-c and 5 b-c resulted, for which NMR data clearly
showed a 2:1 ratio of ocap to added ligand and also coordination of the pyridyl exclu-
sively, with the NH₂ moiety remaining unbound, as shown by the presence of a broad
signal at ca. δ 6 ppm in the ¹H NMR spectra integrating to four protons. Similar reac-
tions were also carried out with 1a but the poor solubility of the products meant that
good quality characterizing data could not be obtained.

2.2. Reactions with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen)
We looked at the reactivity towards 2,2'-bipyridine (bipy) and 1,10-phenanthroline
(phen). Both are excellent chelating ligands and their reactions with mercuric halides
have been widely studied [12–15], with mononuclear complexes of the type [HgX₂(k²-
L₂)] being readily formed [13–16], Two different forms of [HgCl₂(k²-bipy)] have been
crystallographically characterized; the expected mononuclear form and a coordination
polymer [Hg(μ-Cl₂)(k²-bipy)] [13] with 1 D chains containing a distorted octahedral
Hg(II) center resulting from asymmetric bridging of chlorides. Solutions of 1a in EtOH
react with bipy and phen to afford [Hg(SC₆H₃XN(C≡N))(k²-bipy)] (6a) and
[Hg(SC₆H₃XN(C≡N))(k²-phen)] (7a) in good yields (Scheme 3). While NMR spectra are
in full accord with the assigned structures, they are not very informative. Similar reac-
tions with 1b, carried out in refluxing CHCl₃, afforded 6b and 7b, respectively. Here
the methyl group acts as an NMR handle to show a single methyl environment at δ
2.18 and 2.27, respectively, and confirm the ocap and diamine ratio of 1:1. Unfortunately we have been unable to confirm the precise structure using X-ray diffraction despite repeated attempts to grow suitable crystals. We also prepared the chloro- and nitro-derivatives 6c-d and 7c-d, respectively, in the hopes of growing suitable crystals, but again we were unsuccessful.

2.3. Reactions with \( \text{Ph}_3\text{P} = E \) (\( E = \text{O}, \text{S} \))

We next turned our attention to coordination of other potential two-electron donor ligands in the form of \( \text{Ph}_3\text{P} = \text{O} \) and \( \text{Ph}_3\text{P} = \text{S} \), which we hoped would allow us to probe the nature of hard and soft preference for oxygen and sulfur, respectively. Sun and co-workers [17] reported the synthesis and crystal structure of mononuclear \([\text{HgBr}_2(\kappa^3-\text{O} = \text{PPh}_3)_2]\) for which well-defined \( v(P = \text{O}) \) vibrations are observed in the IR spectrum at 1187, 1164 and 1151 cm\(^{-1}\), while the corresponding chloride has also been briefly reported [18].

Addition of ca. 2.5 equivalents of \( \text{Ph}_3\text{P} = \text{O} \) or \( \text{Ph}_3\text{P} = \text{S} \) led to formation of new products 8a-b and 9b,d characterized analytically as adducts with a ratio of Hg to phosphine-chalcogenide of 1:1. For all, a singlet is observed in the \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum, for example at 25.5 ppm for 8a, while for the same complex IR bands at 1166(s) and 1118(s) cm\(^{-1}\) are in accord with the expected positions for \( v(P = \text{O}) \) vibrations. The \(^1\text{H}\) NMR spectra of both 8b and 9b show a single methyl environment at \( \delta \) 2.28 and integration suggests that there is an ocap to added ligand ratio of 1:1 despite the excess of \( \text{Ph}_3\text{P} = E \) used. Once again, our inability to grow suitable single crystals means that the precise molecular structures remain unknown. We favor that shown in Scheme 4 on the basis of the 1:1 ratio of ligands and this structural type is adopted by \( \text{PPh}_3 \) derivatives [7, 8]. Irrespective of the actual molecular structures is the observation that both of these ligands readily bind to Hg(II) but fail to break the mercury-thiolate bridges, similar to the chemistry observed for phosphines.

2.4. Reaction of 1a with HgCl\(_2(\kappa^2\text{-phen})\)

From the preceding sections it is clear that the polymeric nature of 1 can be disrupted upon addition of two-electron donor ligands. Preliminary studies suggest that binuclear complexes are also available following a similar strategy whereby the donor ligand(s) are coordinated to a second metal center. To test this we reacted 1a with [Hg(\(\kappa^2\text{-phen})\)Cl\(_2\)] in EtOH. Both reagents were only sparingly soluble, but a slow deepening of the color suggested that they were slowly reacting. After 2 h a bright yellow
precipitate formed which was collected and dried to afford what we suggest is the unsymmetrical bimetallic \([\text{Hg}\{\kappa^2\text{-SC}_6\text{H}_4\text{N}(C\equiv N)\}(\mu\text{-Cl})_2\text{Hg}(\kappa^2\text{-phen})}\) (10) (Scheme 5).

The \(^1\)H NMR spectrum clearly shows formation of a new product containing equal amounts of phen and ocap ligands, while elemental analysis is consistent with the stoichiometry shown. We have been unable to grow crystals to confirm this formulation but are further developing this concept with the aim of preparing a range of heterobimetallic ocap complexes.

### 3. Summary and conclusion

In this contribution we have prepared and characterized a range of new Hg(II) orthocyanano-aminothiophenolate (ocap) complexes by reaction of the coordination polymers \([\text{Hg}\{\text{SC}_6\text{H}_3\text{XN}(C\equiv N)\}_n]\) with N, O, and S-donor ligands. With both monodentate and bidentate N-donor ligands, mononuclear complexes result in which the ocap ligand binds in a simple chelate fashion through nitrogen and sulfur and the pendent cyanide ligand remains uncoordinated. This contrasts with our earlier investigation of these polymers with mono and bidentate phosphines in which the majority of products were either binuclear ocap-bridged complexes or coordination polymers in which a \(\kappa^3,\kappa^1\)-diphosphine linked Hg(ocap) centers [7, 8]. The predominance of mononuclear species models the chemistry we have recently found with Pd(II)-ocap complexes. In contrast, both Ph\(_3\)P = E (O, S) react in a 1:1 stoichiometry to afford species which we propose on the basis of the analogous PPh\(_3\) chemistry [7, 8] to be ocap-bridged dimers. Somewhat unexpectedly, addition of [HgCl\(_2\)(\(\kappa^2\)-phen)] to [Hg\{\text{SC}_6\text{H}_4\text{N}(C\equiv N)\}_n] also results in breakdown of the polymeric network to afford a bs(chloride)-bridged dimer formulated as [Hg\{\kappa^2\text{-SC}_6\text{H}_4\text{N}(C\equiv N)\}(\mu\text{-Cl})_2\text{Hg}(\kappa^2\text{-phen})]. In the analogous phosphine chemistry [7, 8] we were able to show that, while several species may be
accessible in solution, interconverting via a number of (unresolved) fluxional processes (as evidence by broad NMR spectra), in the solid state a range of different ocap coordination modes were accessible. In marked contrast, all complexes reported here show sharp and well-resolved NMR spectra, in accord with static solution structures (on the NMR timeframe) but frustratingly, we have been unable to unequivocally establish coordination modes due to our inability to grow crystals of suitable quality. Attempts to do this are ongoing as we further develop the coordination chemistry of this novel redox-active ligand.

4. Experimental

4.1. General procedures

$^1$H and $^{31}$P($^1$H) NMR spectra were recorded on a Varian Unity spectrometer. IR spectra were recorded either on a Shimadzu FT-IR 8400 spectrophotometer from 400-4000 cm$^{-1}$ as KBr discs and from 200-600 cm$^{-1}$ as CsI discs or on Bruker Tensor 28 spectrometer with a platinum ATR unit in Martin-Luther Universität Halle-Wittenberg, Germany. Elemental analyses were carried out at Al Al-Bayt University, Jorden using a Euro vector EURO EA300 elemental analyzer. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. All commercially pure chemicals were used as received. Complexes $^{1}$a-d were prepared as previously outlined [8].

4.2. Synthesis of $[\text{Hg}\{\text{SC}_6\text{H}_3\text{XN(C=}\text{N)}\}_2,\text{L}_2]{(2-5)}$

To a suspension of $^{1}$b (0.200 g, 0.554 mmol) in CHCl$_3$ (10 ml), pyridine (py) (0.08 g, 1.108 mmol) was added, and the mixture was refluxed for 3 h. The yellow solution was set aside to slowly evaporate at room temperature. A yellow solid formed which was collected, washed with Et$_2$O and dried under vacuum. Recrystallization from DMSO gave a yellow powder.

$^{2}$b: Yellow, yield: 0.212 g (76%). Anal. Calc. for C$_{18}$H$_{16}$HgN$_4$S: C, 41.50; H, 3.10; N, 10.75. Found: C, 41.63; H, 3.48; N, 10.83%. IR (KBr): 3033w, 2910w, 2136vs, 1620 m, 1596 m, 1529s, 1477s, 1338 m, 803 s, 700 m, 308w, 261w cm$^{-1}$. $^1$H NMR (DMSO-d$_6$): δ 7.42 (s, 1H); 7.29-7.38 (m, 4H, py); 7.19 (d, 1H, J 7.5 Hz); 6.99 (d, 2H, J 7.5 Hz); 6.88-6.95 (m, 6H, py); 2.28 (s, 3H, CH$_3$). Melting point: 195-196 $^\circ$C.

$^{2}$c: Yellow, yield: 0.230 g (77%). Anal. Calc. for C$_{17}$H$_{13}$ClHgN$_4$S: C, 37.71; H, 2.42; N, 10.35. Found: C, 37.83; H, 2.36; N, 10.41%. IR (KBr): 3033w, 2916w, 2137s, 1631 m, 1531s, 1444s, 1053s, 803 s, 759 s, 661 m, 308w, 261w cm$^{-1}$. $^1$H NMR (DMSO-d$_6$): δ 8.57 (d, 4H, J 7.8 Hz, py); 7.78 (t, 4H, J 7.7 Hz, py); 7.55 (s, 2H); 7.37-7.40 (m, 2H, py); 7.14 (d, 1H, J 8.0 Hz); 7.06 (d, 1H, J 7.8 Hz) ppm. Melting point: 185-186 $^\circ$C.

Closely related pyrazole (pz) ($^{3}$b-c), 2-aminopyridine (2-ampy) ($^{4}$b-c) and 2-amino- pyrimidine (2-ampym) ($^{5}$b-c) and complexes were prepared and isolated using similar methods.

$^{3}$b: Yellow, yield: 0.154 g (85%). Anal. Calc. for C$_{14}$H$_{14}$HgN$_4$S: C, 33.70; H, 2.83; N, 16.84. Found: C, 33.83; H, 2.78; N, 17.13%. IR (KBr): 3101w, 2916w, 2137s, 1631 m, 1531s, 1444s, 1053s, 803 s, 759 s, 316w, 279w cm$^{-1}$. $^1$H NMR (DMSO-d$_6$): δ 7.61 (s, 4H,
pz); 7.42 (s, 1H); 7.28 (s, 2H, NH); 7.19 (d, 2H, J 7.9 Hz); 6.99 (d, 1H, J 7.9 Hz); 6.26 (s, 2H, pz); 2.28 (s, 3H, CH3). Melting point: 273-275 °C.

3c: Yellow, yield: 0.163 g (87%). Anal. Calc. for C13H10ClHgN6S: C, 30.12; H, 1.93; N, 16.51%. IR (KBr): 3033w, 2133s, 1579 m, 1531s, 1451s, 1058s, 810 m, 312w, 256w cm⁻¹. ¹H NMR (DMSO-d₆): δ 7.63 (s, 4H, pz); 7.74 (s, 2H, NH); 7.59 (s, 1H); 7.28 (d, 2H, J 7.9 Hz); 7.19 (d, 1H, J 7.8 Hz); 6.29 (s, 2H, pz). Melting point: 273-275 °C.

4b: Yellow, yield: 0.169 g (85%). Anal. Calc. for C18H18HgN6S: C, 39.23; H, 3.29; N, 15.25. Found: C, 39.16; H, 2.23; N, 15.11%. IR (KBr): 3062w, 2914w, 2137s, 1620 m, 1562s, 1444s, 1319s, 1153s, 804 m, 767 s, 345w, 281w cm⁻¹. ¹H NMR (DMSO-d₆): δ 8.09 (d, 2H, apy); 7.54 (t, 2H, apy); 7.42 (s, 1H); 7.21 (d, 1H, J 7.8 Hz); 6.73 (d, 2H, J 7.8 Hz); 6.66 (t, 4H, J 7.8 Hz, apy); 6.02 (s, 2H, NH₂); 2.34 (s, 3H, CH3). Melting point: 159-162 °C.

4c: Yellow, yield: 0.172 g (83%). Anal. Calc. for C17H15ClHgN6S: C, 35.73; H, 2.65; N, 14.71. Found: C, 35.88; H, 2.36; N, 14.61%. IR (KBr): 3055w, 2131s, 1647 m, 1566m, 1461s, 1319s, 1153s, 804 m, 761 s. ¹H NMR (DMSO-d₆): δ 7.88 (d, 2H, apy); 7.49 (s, 1H); 7.41 (m, 3H, apy and E-H); 7.03-7.09 (m, 3H, apy and E-H); 6.52 (d, 2H, J 8.0 Hz, apy); 6.15 (br, 4H, NH₂). Melting point: 261-262 °C (decomposes). (E-H is H of 2-cyanoamino-5-chlorothiophenolate).

5b: Yellow, yield: 0.170 g (85%). Anal. Calc. for C16H16HgN8S: C, 34.75; H, 2.92; N, 20.26. Found: C, 34.85; H, 2.36; N, 20.36%. IR (KBr): 3053w, 2137s, 1647 m, 1568s, 1461s, 1319s, 1153s, 804 m, 761 s. ¹H NMR (DMSO-d₆): δ 8.09 (d, 2H, J 7.8 Hz); 7.54 (t, 2H, J 7.6 Hz); 7.42 (s, 1H); 7.21 (d, 1H, J 7.8 Hz); 6.73 (d, 2H, J 7.8 Hz); 6.66 (t, 4H, J 7.8 Hz, apy); 6.02 (s, 2H, NH₂); 2.34 (s, 3H, CH₃). Melting point: 159-162 °C.

4.3. Preparation of [Hg(SC₆H₃XN(C≡N))(κ²-L)] (6-7)

A solution of 2,2’-bipyridine (bipy) (0.073 g, 0.467 mmol) in EtOH (10 ml) was added to a suspension of 1a (0.162 g, 0.467 mmol) in ethanol (10 ml). The mixture was stirred for 3 h. The yellow precipitate formed was filtered off, washed with EtOH and dried under vacuum to give a yellow powder.

6a: Pale yellow, yield: 0.176 g (75%). Anal. Calc. for C17H12HgN4S·0.2CHCl₃: C, 39.06; H, 2.33; N, 10.59. Found: C, 39.45; H, 2.43; N, 10.55%. IR (KBr): 3053w, 2150vs, 1577 m, 1465vs, 1427 m, 1309 m, 748vs, 723 s cm⁻¹. ¹H NMR (DMSO-d₆): δ 8.69 (d, 2H, J 7.6 Hz, bipy); 8.41 (d, 2H, J 7.4 Hz, bipy); 7.99 (dt, 2H, J 1.8 Hz, bipy); 7.49 (dt, 2H, J 4.8, 1.4 Hz, bipy); 7.44 (d, 1H, J 7.6 Hz); 7.08 (t, J 7.8 Hz, 1H); 7.04 (d, 1H, J 7.0 Hz); 6.64 (t, 1H, J 7.7 Hz) ppm. Melting point: 226-227 °C (decomposes).

A solution of 2,2'-bipyridine (bipy) (0.088 g, 0.554 mmol) in CHCl₃ (10 ml) was added to a suspension of 1b (0.200 g, 0.554 mmol) in CHCl₃ (10 ml). The mixture was refluxed...
for 3 h. The yellow solution was slow evaporated at room temperature giving a yellow precipitate which was filtered, washed with diethyl ether and dried under vacuum. The precipitate was recrystallized from DMF to give a pale-yellow powder. Complexes 6c and 6e were prepared and isolated using a similar method.

6b: Yellow, yield: 0.242 g (68%). Anal. Calc. for C_{18}H_{14}HgN_{4}S: C, 41.66; H, 2.72; N, 10.67%. IR (KBr): 3008 w, 2910 w, 2137 s, 1591 m, 804 m cm\(^{-1}\). \(^1\)H NMR (DMSO-d\(^6\)): \(\delta\) 8.88 (d, 2H, J 8.0 Hz, bipy); 8.65 (d, 2H, J 8.0 Hz, bipy); 8.16-8.20 (m, 2H, bipy); 7.43 (s, 1H); 7.21 (d, 1H, J 7.8 Hz); 6.96 (d, 2H, J 7.8 Hz); 2.18 (s, 3H, CH\(_3\)). Melting point: 176-178°C.

6c: Pale yellow, yield: 0.189 g (75%). Anal. Calc. for C_{17}H_{11}ClHgN_{4}S: C, 37.85; H, 2.06; N, 10.39. Found: C, 38.06; H, 2.17; N, 10.11%. IR (KBr): 3050 w, 2133, 1593 m, 800 m cm\(^{-1}\). \(^1\)H NMR (DMSO-d\(^6\)): \(\delta\) 8.67 (s, 2H, bipy); 8.46 (d, 2H, J 8.0 Hz, bipy); 8.04 (t, 2H, J 8.0 Hz, bipy); 7.55 (s, 2H, bipy); 7.43 (s, 1H); 7.01-7.07 (m, 2H). Melting point: 181-187°C (decomposes).

6d: Yellow, yield: 0.183 g (71%). Anal. Calc. for C_{17}H_{11}HgN_{5}O_{2}S: C, 37.13; H, 2.02; N, 2.73. Found: C, 37.41; H, 2.14; N, 12.82%. IR (KBr): 3055 w, 2975 w, 2140 s, 1587 m, 800 m cm\(^{-1}\). \(^1\)H NMR (DMSO-d\(^6\)): \(\delta\) 8.70 (dd, 2H, J 8.0, 1.6 Hz, bipy); 8.42 (d, 2H, J 7.9 Hz, bipy); 8.21 (s, 1H); 8.10 (d, 1H, J 7.9 Hz); 8.00 (d, 2H, J 7.9 Hz, bipy); 7.50 (dd, 2H, J 7.9, 1.6 Hz, bipy); 7.41 (d, 1H, J 8.0 Hz). Melting point: 296-298°C.

A solution of 1,10-phenanthroline (phen) (0.084 g, 0.465 mmol) in EtOH (10 ml) was added to a suspension of 1a (0.162 g, 0.465 mmol) in ethanol (10 ml). The mixture was stirred for 3 h. The yellow precipitate formed was filtered off, washed with EtOH and dried under vacuum to give a yellow powder.

7a: Yellow, yield: 0.210 g (85%). Anal. Calc. for C_{19}H_{12}HgN_{4}S: C, 43.14; H, 2.29; N, 10.59. Found: C, 42.53; H, 2.19; N, 10.79%. IR (KBr): 3053 w, 2121 vs, 1512 m, 1465 s, 1311 m, 838 m, 748 vs, 723 s cm\(^{-1}\). \(^1\)H NMR (DMSO-d\(^6\)): \(\delta\) 8.83 (d, 2H, J 6.1 Hz, phen); 8.22 (d, 2H, J 7.4 Hz, phen); 8.01 (s, 2H, phen); 7.25 (t, 2H, J 7.4 Hz, phen); 6.91 (d, 1H, J 7.4 Hz); 6.72 (t, 1H, J 7.4 Hz); 6.45 (d, 1H, J 7.5 Hz); 6.38 (t, 1H, J 7.5 Hz) ppm. Melting point: 230-233°C.

A solution of 1,10-phenanthroline (phen) (0.050 g, 0.277 mmol) in CHCl\(_3\) (10 ml) was added to a suspension of 1b (0.100 g, 0.277 mmol) in CHCl\(_3\) (10 ml). The mixture was refluxed for 3 h. The yellow solution was slow evaporated at room temperature giving a yellow precipitate which was filtered, washed with Et\(_2\)O and dried under vacuum. The yellow precipitate was recrystallized from DMF to give a pale-yellow powder.

7b: Yellow, yield: 0.152 g (78%). Anal. Calc. for C_{20}H_{14}HgN_{4}S: C, 44.24; H, 2.60; N, 10.32. Found: C, 44.63; H, 2.81; N, 10.16%. IR (KBr): 3008 w, 2910 w, 2137 s, 1591 m, 804 m cm\(^{-1}\). \(^1\)H NMR (DMSO-d\(^6\)): \(\delta\) 9.11 (d, 2H, J 8.0 Hz, phen); 8.68 (d, 2H, J 8.0 Hz, phen); 8.05 (m, 2H, phen); 7.85-7.88 (m, 2H, phen); 7.41 (s, 1H); 7.27 (d, 1H, J 8.0 Hz); 6.99 (d, 2H, J 8.0 Hz); 2.27 (s, 3H, CH\(_3\)). Melting point: 227-231°C.

7c: Yellow, yield: 0.155 g (77%). Anal. Calc. for C_{19}H_{11}ClHgN_{4}S: C, 40.50; H, 1.97; N, 9.94 Found: C, 40.77; H, 2.08; N, 9.83%. IR (KBr): 3050 w, 2133 s, 1593 m, 800 m cm\(^{-1}\). \(^1\)H NMR (DMSO-d\(^6\)): \(\delta\) 9.13 (s, 2H, phen); 8.70 (t, 2H, J 7.8 Hz, phen); 8.12 (d, 2H, J 9.9 Hz, phen); 7.94-7.99 (m, 2H, phen); 7.55 (s, 1H); 7.28 (d, J 8.0 Hz, 1H); 6.83 (d, 2H, J 8.0 Hz). Melting point: 127-130°C.

7d: Dark yellow, yield: 0.143 g (71%). Anal. Calc. for C_{19}H_{11}HgN_{5}O_{2}S: C, 39.76; H, 1.93; N, 12.20. Found: C, 39.39; H, 2.09; N, 12.32%. IR (KBr): 3055 w, 2990 w, 2140 s, 1607 m,
808 m cm$^{-1}$. $^1$H NMR (DMSO-d$_6$): $\delta$ 8.67 (d, 2H, J 8.0 Hz, phen); 8.42 (d, 2H, J 8.0 Hz, phen); 8.21 (s, 1H); 8.10 (d, 1H, J 8.0 Hz); 8.00 (dd, 2H, J 7.9 Hz, phen); 7.77 (dd, 2H, J 7.9, 1.6 Hz, phen); 7.41 (d, J 7.8 Hz). Melting point: 211-215 °C (decomposes).

4.4. Preparation of $\text{[Hg}\{\text{SC}_6\text{H}_3\text{XN}(\text{C} \equiv \text{N})\}(\text{O} = \text{PPh}_3)]_2$ (8)

A solution of $\text{O} = \text{PPh}_3$ (0.318 g, 1.143 mmol) in CHCl$_3$ (15 ml) was added to a suspension of 1a (0.199 g, 0.571 mmol) in CHCl$_3$ (15 ml). The mixture was stirred at room temperature for 2 h and the yellow solution formed was refluxed for another 2 h. A yellow precipitate formed which was filtered off, dried under vacuum, and then recrystallized from DMSO/CHCl$_3$, to give pale yellow powder of 8a. Complex 8b was prepared and isolated using a similar method.

8a: Pale yellow. Yield: 1.064 g (94%). Anal. Calc. for C$_{50}$H$_{38}$Hg$_2$N$_4$O$_2$P$_2$S$_2$: C, 47.88; H, 3.05; N, 4.47. Found: C, 48.23; H, 3.17; N, 4.42%. IR (KBr): 3053w, 2115s, 1465 m, 1436 m, 1166s, 1118s, 750 m, 696 s, 541vs cm$^{-1}$. $^1$H NMR (DMSO-d$_6$): $\delta$ 6.74 (t, 1H, J 7.5 Hz); 7.10 (d, 1H, J 7.5 Hz); 7.14 (t, 1H, J 7.4 Hz); 7.54-7.65 (m, 16H) ppm. $^{31}$P $^1$H NMR (DMSO-d$_6$): $\delta$ 25.5 (s) ppm. Melting point: 131-134 °C.

8b: Yellow, yield: 0.162 g (86%). Anal. Calc. for C$_{50}$H$_{36}$Hg$_2$N$_6$O$_6$P$_2$S$_2$: C, 44.68; H, 2.70; N, 6.25. Found: C, 44.61; H, 2.65; N, 6.42%. IR (KBr): 3059w, 2937w, 2147s, 1529 m, 1436s, 1178s, 1118s, 752 s, 692 s, 536vs, 503 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 2.28 (s, 3H, CH$_3$); 6.90-6.96 (m, 2H); 7.42 (s, 1H); 7.52-7.82 (m, 15H, Ph) ppm. $^{31}$P $^1$H NMR (CDCl$_3$): $\delta$ 40.3 (s) ppm. Melting point: 123-127 °C.

4.5. Preparation of $\text{[Hg}\{\text{SC}_6\text{H}_3\text{XN}(\text{C} \equiv \text{N})\}(\text{S} = \text{PPh}_3)]_2$ (9)

A solution of S = PPh$_3$ (0.162 g, 0.552 mmol) in CHCl$_3$ (15 ml) was added to a suspension of 1b (0.100 g, 0.276 mmol) in CHCl$_3$ (15 ml). The mixture was stirred at room temperature for 2 h and the dark yellow solution formed was refluxed for another 2 h. A dark yellow precipitate formed which was filtered off, dried under vacuum, and then recrystallized from DMSO/CHCl$_3$, to give dark yellow powder of 9b. Complex 9d was prepared and isolated using a similar method.

9b: Dark yellow, yield: 0.189 g (75%). Anal. Calc. for C$_{52}$H$_{42}$Hg$_2$N$_4$P$_2$S$_4$: C, 47.52; H, 3.22; N, 4.26. Found: C, 47.37; H, 2.99; N, 4.38%. IR: 3078w, 2931w, 2147s, 1543 m, 1431s, 511 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 2.28 (s, 3H, CH$_3$); 6.89-6.95 (m, 2H); 7.37 (s, 1H); 7.51-7.77 (m, 15H, Ph) ppm. $^{31}$P $^1$H NMR (CDCl$_3$): $\delta$ 45.5 (s) ppm. Melting point: 155-156 °C.

9d: Pale yellow, yield: 0.163 g (78%). Anal. Calc. for C$_{50}$H$_{36}$Hg$_2$N$_4$O$_4$P$_2$S$_4$: C, 44.54; H, 2.69; N, 4.16. Found: C, 44.67; H, 2.71; N, 4.38%. IR (KBr): 3068w, 2139s, 1465 m, 1434s, 1292vs (NO$_2$), 490 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 7.11-7.83 (m, 18H, Ph and H) ppm. $^{31}$P $^1$H NMR (CDCl$_3$): $\delta$ 13.6 (s) ppm. Melting point: 236-238 °C (decomposes).

4.6. Preparation of $\text{[Hg}\{\text{SC}_6\text{H}_4\text{N}(\text{C} \equiv \text{N})\}\text{HgCl}_2(\kappa^2\text{phen})]$ (10)

A white suspension of [Hg(κ$^2$-phen)Cl$_2$] (0.100 g, 0.074 mmol) in ethanol (10 ml) was added to a suspension of 1a (0.074 g, 0.212 mmol) in ethanol (10 ml). The mixture was
stirred at room temperature for 2 h. The yellow precipitate which formed was filtered off, washed with ethanol and dried under vacuum to give a yellow powder.

10: Yellow, yield 0.123 g (78%). Anal. Calc. for C_{19}H_{12}Cl_{2}Hg_{2}N_{4}S: C, 28.51; H, 1.51; N, 7.00. Found: C, 28.77; H, 1.68; N, 6.83%. IR (KBr): 3055 m, 2123vs, 1517s, 1467s, 1427s, 844vs, 748 s, 721 s cm^{-1}. ^{1}H NMR (DMSO-d_{6}): δ 8.93 (d, 2H, J 6.0 Hz, phen); 8.32 (d, 2H, J 7.4, phen); 7.81 (s, 2H, phen); 7.04 (t, 2H, J 7.4 Hz, phen); 6.71 (d, 1H, J 7.6 Hz); 6.52 (t, 1H, J 7.4 Hz); 6.25 (d, 1H, J 7.4 Hz); 6.18 (t, 1H, J 7.4 Hz) ppm. Melting point: 278-282 °C (decomposes).

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Disclosure statement

There are no conflicts of interest to declare.

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