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Short Communication

Mixed Ligand of Mercury (II) Complexes of 4-Flouro-2-Cyanoaminothiophenolate with Amine or Triphenylphosphine as Co-Ligand

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ABSTRACT

The coordination chemistry of benzothiazole and its derivatives with mercury (II) has been in focus because of the prominent role it plays in biological systems. This study was aimed at synthesizing and characterizing some new complexes of mercury (II) with mixed ligands of 4-flouro-2-cyanoaminothiophenolate and 2,2'-bipyridine, 1,10-phenanthroline, ethylenediamine, 2-aminopyridine, 2-amino-3-methyl-pyridine or triphenylphosphine. The complexes were synthesized and characterized using the infrared spectrophotometry and nuclear magnetic resonance (NMR). Melting point and conductivity were measured on Gallenkamp melting point-device and digital conductivity meter, respectively. The results showed that the 2-cyanoaminothiophenolate ligand was bonded through the nitrogen of amino group and sulfur atoms. The diamine ligands (en, Phen, Bipy) were coordinated as bidentate, chelating through the nitrogen atoms, while the mono amine (2-amino pyridine, 2-amino-3-methylpyridine) were coordinated through the nitrogen of the heterocyclic ring, to afford a tetrahedral geometry around the Hg(II) ion.

Keywords: Heterocyclic amines, Mercury (II) complex, NMR, Spectra, 4-flouro-2-cyanoaminothiophenolate.

Introduction

The biochemistry of mercury-amino-thiolite has been found exciting and the compound has been proven to have several advantages in the last fifty years, owing to the existence of sulfur and nitrogen compounds in biological systems. Mercury is known for the formation of steady complexes in conjunction with thiols.[1] 2-aminobenzothiazole and its complexes with different metal ions such as mercury, palladium have been reported[2] and have played a remarkable role in spectrometry and polarography.[3,4] Attention in coordination chemistry of benzothiazole and its derivatives with mercury (II) has been raised because of the prominent role it plays in biological systems.[6,5] Thiols have strong affinities to combine with soft metals, and there are several synthetic complexes of this kind of compounds.[7] These ligands provide rigid donor atoms (like O and N) and are significant in coordination chemistry.[8] The state of hard and soft donor atoms gives considerable opportunities for bonding with various transition metals.[9,10] Some thiols containing functional groups (i.e., penicillamine [3-sulfanyl-D-valine]) are utilized in the remediation of heavy metal toxicity via the formation of complexes with them (anticancer efficiency).[11]

Heterocyclic aromatic ligands are the main type of ligands in coordination chemistry.[12] Monodentate ligands (i.e., pyridine, pyridine pyridine or triphenylphosphine derivatives) and chelating ligands (i.e., 2,2'-bipyridine and 1,10-phenanthroline) are stable complexes with most transition metal ions and have been widely used in both analytical chemistry and introductory chemistry. The heterocyclic compounds with six-membered aromatic nitrogen are comparatively weak energy orbitals, which are well receptors for electronic densities of metal d-orbital electron intensity in reverse-metal bonding (metal-ligand back bonding). Conversely, the five-membered aromatic nitrogen heterocycles are good N-donors. They can be found in the form of negative ligands via removing the acidic hydrogen atom in free ligand.[12,13] The significance and feature of sulfur, nitrogen, and phosphorus as donating atoms to other traditional ligands and phosphates are owing to their capacity to form stable and soluble compounds.[14-17] The aims of the present research were to synthesize and characterize some new complexes of mercury (II) with mixed ligands of 4-flouro-2-cyanoaminothiophenolate, 2,2'-bipyridine, 1,10-phenanthroline, ethylenediamine, 2-aminopyridine, 2-amino-3-methyl-

Materials and Methods

Source of chemical reagents

Mercury (II) acetate (HgOAc), 2,2'-bipyridine (bipy), 1,10-phenanthrolien (Phen), ethylenediamine (en), 2-amino-3-methylpyridine (ammpy), 2-aminopyridine (ampy) and triphenylphosphine (PPh_3) were purchased and utilized as supplied.

Characterization of complexes

Infrared spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer. ^1H NMR spectra were recorded on Varian Gemini 400 (400 MHz) spectrometer in DMSO-d_6 as the solvent. Melting points were measured on Gallenkamp melting point-device. Conductivity measurements were carried out on a digital conductivity meter using 10^{-3}M DMSO solution.

Synthesis of 4-flouro-2-cyanoaminothiophenolate

To synthesize 4-flouro-2-cyanoaminothiophenolate, 10.1 g (0.1 mol) of 4-flouroaniline in 25 mL glacial acetic acid was added to a solution of 38.8 g (0.4 mol) of potassium thiocyanate in 70 ml glacial acetic acid and placed in a round-bottom flask fitted with an efficient

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mechanical stirrer and reflux condenser. The mixture was cooled in an ice-salt mixture until the temperature decreased to about 0 - 5 ^{o}C, and then 6.5 mL Br_2 solution was added to 30 mL glacial acetic acid. After the bromination was completed, the mixture was kept overnight at room temperature**.** A light orange precipitate was obtained at the bottom of the flask, after which 25 mL of hot water was added. The mixture was heated to 85^{o}C and filtered hot. The orange precipitate was put in a conical flask, treated with 10 mL acetic acid and heated to 85°C, and the mixture was filtered. The product obtained was cooled, filtered and made alkaline with concentrated ammonia solution to a pH range of 6.0-7.0. Then, the pale-yellow precipitate was collected, filtered and washed with water. Recrystallization from glacial acetic acid was carried out, followed by washing with water, methanol (75%) to afford 4-flouro-2-aminebenzothiazole (m.p. 187-190 °C, 89 % yield).

Synthesis of thiolate complex $[Hg(A)]_n$ *(*A^{2-} *= 4-flouro-2-cyanoaminothiophenolate)*

A solution of 4-fluorobenzo[d]thiazol-2-amine (0.789 g, 4.696 mmol) in 10 mL of 95 % ethanol was added to a solution of mercury (II) acetate (1.520 g, 4.769 mmol) in 10 mL 95 % ethanol with stirring to form a yellow precipitate directly. The mixture was stirred, refluxed for two hours, filtered off, and air dried. The product was recrystallized from DMSO to give white solid (1.481 g, 86 % yield).

Synthesis of [Hg(A)(bipy)] complex

A solution of bipy (0.249 g, 1.594 mmol) in 10 mL of 95 % ethanol was added to a suspension of $[Hg(A)]_n$ (0.554 g, 1.510 mmol) in 8 mL of 95 % ethanol with stirring. The mixture was refluxed for two hours, then cooled to room temperature. The white precipitate products were filtered off and air dried (0.352 g, 45 % yield).

Synthesis of [Hg(A)(phen)] complex

The complex [Hg(A)(phen)] was prepared and isolated using a similar procedure used for the synthesis of [Hg(A)(bipy)] complex (0.28 g, 56 % yield).

Synthesis of [Hg(A)(en)] complex

Suspension of $[Hg(A)]_n$ (0.200 g, 0.545 mmol) in 10 mL of ethanol (95%) was added to a solution of ethylenediamine (0.034 g, 0.566 mmol) in 5 mL of ethanol (95%) with stirring, no change was observed. Then, the mixture was refluxed for two hours, cooled to room temperature, filtered off and air-dried (0.105 g, 58 %).

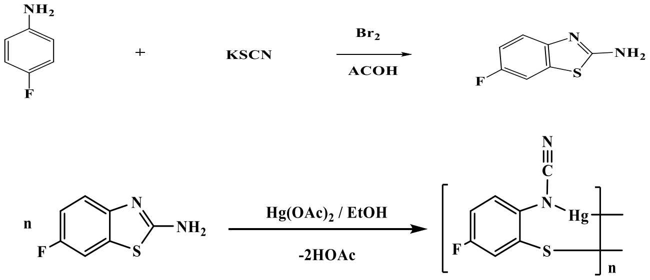
Synthesis of $[Hg(A)(ampy)_2]$*,* $[Hg(A)(ammpy)_2]$ *and* $[Hg(A)(PPh_3)_2]$ *complexes*

The complexes $[Hg(A)(2\text{-}ampy)_2]$, $[Hg(A)(ammpy)_2]$ and $[Hg(A)(PPh_3)_2]$ were prepared and isolated using a similar procedure used for synthesizing [Hg(A)(en)] complex; {$[Hg(A)(ampy)_2]$ (0.133 g, 29 % yield); $[Hg(A)(ammpy)_2]$ (0.151 g, 47 % yield); $[Hg(A)(PPh_3)_2]$ (0.250 g, 53 % yield)}. mercury through nitrogen atom.[22-24] Strong bands at 773-774 cm^{-1} were due to CH deformation of ligand bip**y**; also bands at 732-714 cm^{-1} and 856-849 cm^{-1} were owing to CH deformation of ligand Phen in the [Hg(A)(bipy)] and [Hg(A)(phen)] complexes.[25]

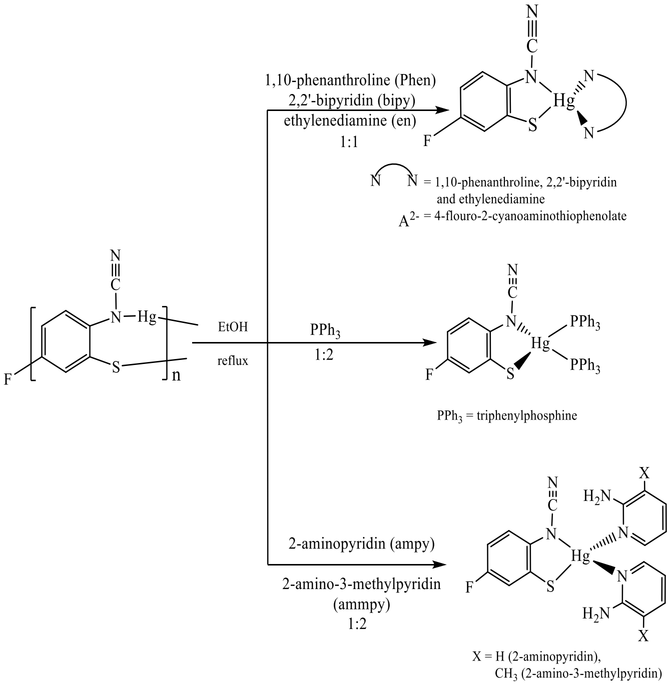
Results and Discussion

Addition of 2-amino-6-fluorobenzothiazole to mercury acetate in ethanol led to the configuration of complex 1 and based on analytical and spectral data, the complex formula was assumed to be $[HgA]_n$ (Scheme 1). This type of complex was prepared and confirmed for the first time by Aljibori et al.[18] The prepared complex was more stable in air and dissolved in DMSO and DMF solvents. Characterization of the complex was carried out by elemental analysis, ^{1}H NMR, infrared (IR), and electrical conductivity. The complex formed was reacted with two groups: the first group was chelating amine ligands, ethylenediamine (en), 2,2-dipridine (Bipy), 1.10-phenanthroline (Phen), and the second group was monodentate heterocyclic amines, such as 2-amino-pyridine (ampy) and 2-amino-3-methyl-pyridine (ammpy). In addition, complex $[HgA]_n$ reacted with triphenylphosphine (PPh_3) to give a complex of the type $[Hg(A)(PPh_3)_2]$. The results of analytical data including colour, product, melting point/decomposition, and molar conductivity are shown in Table 1. All the prepared complexes are soluble in DMSO and DMF but are insoluble in other common solvents (Such as EtOH, MeOH and acetone). These prepared complexes were studied and characterized using elemental analysis, infrared spectroscopy, nuclear magnetic resonance, and molar conductivity. Selected bands of the IR are listed in Table 2. The precise analysis of the elements of the prepared compounds corresponds to the calculated values and the basic infrared spectra as shown in Table 1.

Infrared studies on 2-amino-6-fluorobenzothiazole showed that the NH_2 band disappeared from the compound after its reaction with mercury acetate and a new signal band appeared at 2101 cm^{-1} due to $C\equiv N$.[19] This band did not change its position for most of the adduct compounds with a reference that the cyanide group was not associated with mercury.[20,21] The ν(C=C) of most adduct compounds were observed at higher frequencies relative to the parent compounds. The frequency of ν(C=N) showed at 1625 cm^{-1} in the prepared complexes,



Scheme 1: Preparation of 4-flouro-2-aminebenzothiazole and $[Hg(A)]_n$ complex



Scheme 2: Preparation of [Hg(A)(Phen)], [Hg(A)(bipy)], [Hg(A)(en)], $[Hg(A)(PPh_3)_2]$, $[Hg(A)(ampy)_2]$ and $[Hg(A)(ammpy)_2]$ complexes

this band was shifted towards a lower frequency compared to free ligand, and this was in agreement with diamine ligands coordinated to mercury through nitrogen atom.[22-24] Strong bands at 773-774 cm^{-1} were due to CH deformation of ligand bip**y**; also bands at 732-714 cm^{-1} and 856-849 cm^{-1} were owing to CH deformation of ligand Phen in the [Hg(A)(bipy)] and [Hg(A)(phen)] complexes.[25]

The symmetrical and asymmetric NH$_2$ absorption frequency of ethylendiamine was clearly shown to be moderate to weak band at 3360-3250 cm^{-1}, which was shifted towards a lower frequency compared to free ligand.[26]

The spectrum of [Hg(A)(ampy)$_2$] complex showed a band towards a higher frequency of ν(NH$_2$), which were referred to ligand amp**y**. It appeared in the complex at 3220 cm^{-1} and 3394 cm^{-1}. In contrast, its location in free ligand which appeared at 3302 cm^{-1}, this indicated that don't shared in the coordination, while the frequency of ν(C=N) group appeared at the 1595 cm^{-1} compared with free ligand that showed at 1660 cm^{-1}. This shift indicated that the ligand amp**y** coordinates by a nitrogen atom ring.[24,27] The frequency of ν(NH$_2$) also showed in the spectrum of [Hg(A)(ammpy)$_2$] complex towards frequencies 3285 cm^{-1} and 3325 cm^{-1}. At the same time, the frequency of (C=N), inside the ring was shifted to a lower frequency as it appeared in the ligand (ammpy) at 1635 cm^{-1}, compared with product complex that showed at 1595 cm^{-1}, indicating that the (ammpy) was bonded through the endocyclic nitrogen atom.[28] The infrared spectrum of the triphenylphosphine complex showed influential and characteristic bands at 1434, 1100, and 693 cm^{-1} due to the absorption frequency of ν(P-Ph) and ν(P-C) respectively.[29-31]. We noticed that there was a ν(C≡N) band in all the complexes prepared within the range of 2096-2151cm^{-1}, which didn't change in position or little change occurring, indicating that it was not affected and did not engage in the bonding after the interaction of complex [Hg(A)]$_n$ with other adducts.

In the ^{1}H-NMR spectrum of [Hg(A)(phen)] (Figure 1), protons of the phen ligand showed as a doublet peak at 8.96 ppm and was assigned to protons at position 1,1’, doublet at 8.09 ppm was assigned to H3,3’ protons, triplet at 7.43 ppm was assigned to H2,2’ protons and a singlet at 7.85 ppm was assigned to H4,4’ protons. Also the spectrum displayed the protons of A^{-2} ligand and appeared as three peaks; a doublet peak at 8.59 ppm assigned to proton Ha, doublet at 6.95 ppm assigned to Hb proton and singlet at 7.10 ppm assigned to Hc proton.

The ^{1}H-NMR spectrum of [Hg(A)(bipy)] displayed various peaks in the range of 8.72-7.66 ppm belonging to eight protons of bipy ligand and three protons of the aromatic ring of A^{2-} ligand, as indicated from integration. The width of peaks was due to weak solubility of the complex. The ^{1}H-NMR spectrum of [Hg(A)(en)] complex (Fig. 2) displayed the protons of A^{2-} ligand as a multiple peak within 7.56-6.66 ppm range. Also the spectrum showed a broad peak at 4.19 ppm assigned to protons of NH$_2$ group and a single peak at 2.82 ppm assigned to CH$_2$ protons as indicated from integration. The ^{1}H-NMR spectrum of [Hg(A)(ampy)$_2$] complex showed multiple peaks in the range of 7.73-6.70 ppm attributed to eight protons of two aromatic rings of ampy ligand and three protons attributed to aromatic protons of A ligand. The NH$_2$ protons appeared as a single broad peak at 5.98 ppm. The ^{1}H-NMR spectrum of [Hg(A)(ammpy)$_2$] complex showed multiple peaks in the range of 7.74-6.56 ppm due to the six protons of phenyl rings in the ammpy ligand and three protons in A^{-2} ligand. The protons of NH$_2$ group appeared as single broad peak at 6.21 ppm, and the protons of two CH$_3$ groups appeared at 2.06 ppm of the ammpy ligand. Similarly, the ^{1}H-NMR spectrum of [Hg(A)(PPh$_3$)$_2$] complex showed the protons of the phenyl rings in A^{2-} and PPh$_3$ ligands as a multiple peaks within 6.65-7.63 ppm.

Table 1: Analytical and physical properties of synthesized complexes

Compound	M.Wt.	Colour	M.P. (°C)	Yield (%)	C	H	N	Conductivity
[Hg(A)]$_n$	366.76	Dark yellow	247-250*	86	23.01 (22.92)	1.21 (1.16)	7.34 (7.64)	0.35
[Hg(A)(Bipy)]	522.95	Greenish yellow	207-210*	45	38.95 (39.05)	1.95 (2.12)	10.45 (10.71)	7.78
[Hg(A)(Phen)]	546.97	Light orange	232-234	56	41.83 (41.72)	2.15 (2.03)	10.36 (10.24)	8.17
[Hg(A)(en)]	424.85	Light yellow	202-204	58	25.23 (25.44)	2.07 (2.14)	13.32 (13.19)	2.41
[Hg(A)(PPh$_3$)$_2$]	629.06	Light yellow	215-217	53	47.17 (47.73)	3.01 (2.88)	4.55 (4.45)	1.87
[Hg(A)(ampy)$_2$]	555.00	Greenish yellow	240-243*	29	36.41 (36.79)	2.31 (2.72)	15.35 (15.14)	9.12
[Hg(A)(ammpy)$_2$]	583.00	Dark yellow	270-273*	75	39.33 (39.14)	3.19 (3.28)	14.11 (14.41)	7.31

*: Decomposition; M.Wt.: Molecular weight; M.P.: Melting point

Table 2: IR spectra of $[HgA]_n$ and its adducts

Complexes	**ν(C-H)** aromatic **(w)**	**ν(C≡N) (s)**	**ν(C=N) (m)**		**ν(C=C) (s)**	**ν(C-S)**
$[Hg(A)]_n$	3066	2101	---		1479	746s
[HgA(Bipy)]	3045	2096	1597		1481	769m
[HgA(Phen)]	3053	2121	1512		1465	748s
[HgA(en)]	3074	2095	1595		1479	760m
[HgA(ampy)]	3085	2096	1595		1479	770w
[HgA(ammpy)]	3075	2098	1595		1481	760w
			□(P-Ph)	□(P-C)		
$[Hg(A)(PPh_3)_2]$	3052	2125	1434s	1100s 693s	1472	746s

Conclusion

The mixture of heterocyclic amines and triphenylphosphine ligands, coordinated with $[Hg(A)]_n$ led to tetrahedral complexes as follows: The coordination of $[Hg(A)]_n$ with 1,10-phenanthroline, 2,2'-bipyridine and ethylenediamine produced the complexes [Hg(A)(Phen)], [Hg(A)(bipy)] and [Hg(A)(en)] in which both diamines and 4-flouro-2-cyanoaminothiophenolate (A^{2-}) acted as bidentate ligands and the diamines were bonded through nitrogen atoms to form tetrahedral complexes around the Hg(II) ion. In addition, the coordination of $[Hg(A)]_n$ with 2-aminopyridin and 2-amino-3-methylpyridin exhibited the two complexes $[Hg(A)(ampy)_2]$ and $[Hg(A)(ammpy)_2]$, the A^{2-} ligand was bonded with Hg(II) through nitrogen of amino group and sulfur of thiolato groups, while ampy and ammpy ligands were bonded through the nitrogen atom of the heterocyclic ring . Also, the reaction of $[Hg(A)]_n$ ion with triphenylphosphine created the complex $[Hg(A)(PPh_3)_2]$, PPh_3 ligand bonded to mercury (II) ion through phosphorus donor atom.

Conflict of interest

The authors declare no conflict of interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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