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The influence of benzaldehyde-N-alkyl-thiosemicarbazones on the synthesis of gold(I) ionic complexes: Spectroscopy, ESI-mass, structures and variable H-bonded polymeric networks

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ABSTRACT

The effect of the substituents at the N^1/C^2 atoms of the thiosemicarbazones $R^1R^2C^2 = N^3\text{-}N^2H\text{-}C^1(=S)\text{-}N^1HR^3$ on the type of gold(I) complexes is investigated. Direct reaction of gold(I) chloride with benzaldehyde-N-methyl thiosemicarbazones (HL^1: R^1 = Ph, R^2 = H, R^3 = Me) in a 1:2 M ratio in acetonitrile has yielded an ionic complex, $[Au(\kappa^1\text{-}S\text{-}HL^1)_2]Cl$ (**1**). Similarly, the reaction of benzaldehyde-N-ethyl thiosemicarbazone (HL^2: R^1 = Ph, R^2 = H, R^3 = Et) has formed another ionic complex, $[Au(\kappa^1\text{-}S\text{-}HL^2)_2]Cl$ (**2**). The complexes have been characterized using analytical data, spectroscopy (IR, ^1H, ^{13}C NMR, UV–Vis), fluorescence, ESI-mass and X-ray crystallography. Complexes **1** and **2** represent the first examples obtained from the direct reactions of gold(I) chloride with a thio-ligand without the presence of PPh_3 or the use of any intermediate substrate, as has normally been used. Complex **1**, with a methyl substituent at N^1, has two independent molecules in the crystal lattice, while complex **2**, with an N-ethyl substituent, has only one type of molecule in the crystal lattice. ESI-mass studies reveal the formation of the species: $[Au^ICl+H]^+$ (**A**), $[Au^ICl_2(HL^1)+2H]^+$ (**B**), $[Au^I(HL^1)_2]^+$ (**C**) (complex **1**) and $[Au^I(HL^2)_2\text{-}4H]^+$ (**D**) (complex **2**). Interestingly both complexes have shown intense fluorescence bands in the wide region 340–540 nm, corresponding to the excitation wavelength of 308 nm.

1. Introduction

Gold-sulfur compounds find applications in medicine and modern technology. In this respect, gold(I) compounds are found to be suitable in rheumatoid arthritis and anticancer treatments, used in the photographic industry [1], rich in luminescent properties [2] and act as optical [3] and chemosensors [4]. Further, it is found that gold(III) compounds also display antitumor properties similar to cisplatin [5]. Gold(I) compounds display intra- and/or intermolecular d^{10}–d^{10} interactions that assist in modulating their luminescent {due to the metal-centered Au(5d) → Au(6p) transition} and solid state behavior [1–5].

The chemistry of N, S-donor ligands based on thiosemicarbazones $\{(R^1R^2C^2 = N^3\text{-}N^2H\text{-}C^1(=S)\text{-}N^1R^3R^4\}$, an important class of biochemically active molecules [6,7], with gold(I) [8–16] and gold(III) [10,12,17–21] has been investigated to a limited extent compared to other metals [6]. Apart from supramolecular networks, the interest in gold–thiosemicarbazone chemistry has focused on the biochemical and luminescent properties [8–16]. Some of gold(III) complexes have been tested for their in vitro cytotoxic activity against tumor cell lines [18]. Likewise, gold(I)-thiosemicarbazone complexes have been tested for their in vitro cytotoxic activity against tumor cell lines [8], human leukemia and solid tumor cell lines [13], and the human cervix carcinoma cell line [10,15]. It is noted that gold(I) complexes have greater activity than the corresponding gold(III) complexes [10,15].

We have been interested in the coordination chemistry of thiosemicarbazones [22–24] and it has been observed that the substituents at the C^2 and N^1 atoms, as well as variations in the halide ions, the nature of the co-ligand and solvents, all play an important role in controlling the bonding and nuclearity of the resulting complexes. Some of the novel features observed are cyclometallation (Pd, Pt, Ru), variable bridge bonding between metal centers, bond isomerism, multiple bridging, formation of cis–trans isomers, furan oxygen coordination etc [22–24]. In continuation of our interest in metal-thiosemicarbazone chemistry, we reported the first ionic gold(I) complex, $[Au(\kappa^1\text{-}S\text{-}HL^3)_2]Cl$, formed from the direct reaction

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of gold(I) chloride with 3-nitrobenzaldehyde thiosemicarbazone (Chart 1) in the presence of PPh_3 [9]. However, in the literature, complexes have been prepared using different methods that have involved the reaction of a thiosemicarbazone with: (a) $AuCl(PEt_3)$ [8], (b) [AuCl(2,2′-thiodiethanol)] [11,12,15,16], (c) $HAuCl_4$ [13] and $[Au^{III}(damp\text{-}C,N)Cl_2]$ [10,14] as intermediate substrates. The complexes are ionic or neutral and their central cores are enumerated as follows: $[S\text{-}Au\text{-}P]^{n+}$ (n = 1, mononuclear [8], n = 2, dinuclear [15]), $[S\text{-}Au\text{-}S]^{n+}$ {n = 1, mononuclear [9,12,14], n = 3, mononuclear (pyridyl protonated) [12], n = 2, dinuclear [10]}, $[S\text{-}Au\text{-}Cl]^{n+}$ {n = 0, mononuclear [13], n = 1, mononuclear (pyridyl protonated) [13]}, [Cl-Au-S∩P-Au-Cl] [11], [Cl-Au-P∩S-Au-S∩P-Au-Cl] [11] and [S-Au-P_2∩S-Au-P_2] [16]. In view of our interest in preparing gold(I) ionic complexes, the N^1-substituted thiosemicarbazones HL^1 and HL^2, as shown in Chart 1, were reacted directly with gold(I) chloride, without using an intermediate substrate [12,14] or the presence of PPh_3 [9].

2. Materials and techniques

Gold(I) chloride, benzaldehyde, 3-methyl thiosemicarbazide and 3-ethyl thiosemicarbazide were procured from Aldrich Chemicals Ltd., and used as received. Benzaldehyde-N^1-methyl thiosemicarbazone and benzaldehyde-N-ethyl thiosemicarbazone were prepared by refluxing benzaldehyde with the respective thiosemicarbazide in methanol for 8–10 h. 2-Acetylpyridine thiosemicarbazone and salicylaldehyde thiosemicarbazone were prepared using literature methods [25]. The gold(I) complex $[Au(PPh_3)Cl]$ was prepared by a literature method [26]. The C, H and N analyses were obtained with a Thermoelectron FLASHEA1112 CHNS analyzer. Infrared spectra were recorded from KBr pellets in the range 4000–200 cm^{-1} on a Pye–Unicam SP-3-300 spectrophotometer. Melting points were determined with an electrically heated Gallenkamp apparatus. The ^1H NMR spectra were recorded on a Bruker Avance-III 500 spectrometer operating at a frequency of 500 MHz using $CHCl_3$-d as the solvent with TMS as the internal standard and ^{13}C NMR spectra were recorded at an operating frequency of 125 MHz in the same solvent as above (see Chart 2 for the numbering of the C and H atoms). The mass spectra were recorded using DMSO solvent on a Bruker Daltonik LS–MS high resolution microTOF-Q II 10356. The UV–Vis spectra of the ligands and complexes were recorded in methanol solvent with the help of a UV-1601 PC Shimadzu spectrophotometer. Fluorescence spectra of complexes were recorded in methanol solvent with a Varian Cary Eclipse Fluorescence spectrophotometer.

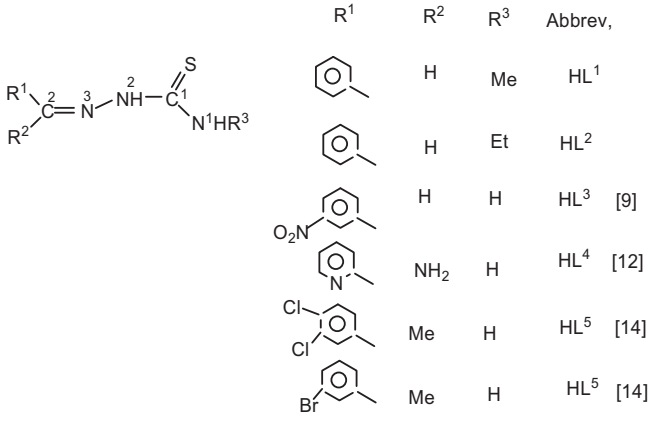

Chart. 1. Thiosemicarbazone ligands under study.

Table 1
Crystallographic data of complexes **1** and **2**.

Empirical formula	$C_{18}H_{22}AuN_6S_2Cl$	$C_{20}H_{26}AuN_6S_2Cl$
M	618.95	647.00
T (K)	110 (2)	110 (2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	15.111	12.2045 (2)
b (Å)	12.921	12.8030 (2)
c (Å)	25.343	15.8333 (3)
α (°)	90.00	90.00
β (°)	105.97	95.1806 (16)
γ (°)	90.00	90.00
V (Å^3)	4757.1	2463.91 (7)
Z	8	4
D_{calc} (g cm^{-3})	1.728	1.744
μ (mm^{-1})	6.488	6.267
Reflections collected	15600	17474
Unique reflections	8688 [R_{int} = 0.0000]	8176 [R_{int} = 0.0253]
Reflections with [$I > 2\sigma(I)$]	8688	6103
Final R indices [$I > 2\sigma(I)$]	R = 0.0483	R = 0.0232
	wR = 0.0884	wR = 0.0431

Table 2
Important bond parameters {bond lengths (Å) and bond angles (°)}.

$[Au(\eta^1\text{-S-Hbtsc-N-Me})_2]Cl$ (**1**)			
Au(1)–S(1B)	2.2760(14)	N(1A)–C(1A)	1.442(6)
Au(1)–S(1A)	2.2839(14)	S(1B)–Au(1)–S(1A)	171.80(5)
Au(2)–S(1D)	2.2686(15)	S(1D)–Au(2)–S(1C)	170.95(6)
Au(2)–S(1C)	2.2717(16)	C(2A)–S(1A)–Au(1)	104.87(17)
S(1A)–C(2A)	1.729(6)	C(2B)–S(1B)–Au(1)	106.80(19)
S(1B)–C(2B)	1.722(5)	C(2C)–S(1C)–Au(2)	105.13(19)
S(1C)–C(2C)	1.727(5)	C(2D)–S(1D)–Au(2)	109.57(18)
S(1D)–C(2D)	1.731(5)	C(2A)–N(1A)–C(1A)	123.3(5)
N(1A)–C(2A)	1.313(6)	C(2A)–N(2A)–N(3A)	119.1(4)
$[Au(\eta^1\text{-S-Hbtsc-N-Et})_2]Cl$ (**2**)			
Au–S(1A)	2.2822(6)	S1(A)–Au–S(1B)	168.33(2)
Au–(S1B)	2.2828(6)	C(3A)–S(1A)–Au	106.38(8)
S1A–C(3A)	1.730(2)	C(3B)–S(1B)–Au	106.54(8)
S1B–C(3B)	1.727(2)	C(3A)–N(1A)–C(2A)	125.5(2)
N1A–C(3A)	1.327(3)	C(4A)–N(3A)–N(2A)	115.74(17)
N1A–(C2A)	1.472(3)		

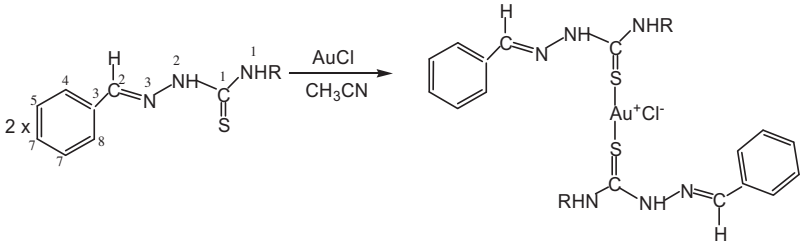

Chart. 2. Synthesis of complexes, R = Me, 1; Et, 2.

2.1. Synthesis of the complexes

2.1.1. Synthesis of $[Au(\kappa^1\text{-}S\text{-}HL^1)_2]Cl$ (**1**)

Gold(I) chloride (0.025 g, 0.107 mmol) was suspended in 15 mL of acetonitrile, the thio-ligand HL^1 (0.041 g, 0.214 mmol) was added and the reaction mixture was stirred for 2 h. The light yellow clear solution that formed was filtered and kept for crystallization. Slow evaporation at room temperature yielded crystals of $[Au(\kappa^1\text{-}S\text{-}HL^1)_2]\cdot Cl$ (**1**) (0.042 g, 63%; mp 202–204 °C). *Anal.* Calc. for $C_{18}H_{22}N_6S_2AuCl$: C, 34.92; H, 3.55; N, 13.60. Found: C, 34.86; H, 3.56; N, 13.71%. Main IR bands (KBr, cm^{-1}): $\nu(N^1\text{–}H)$ 3371m, 3273m; $\nu(\text{–}N^2H\text{–})$ 3122m; ν(C–H) 3071br, 2975m, 2940m; ν(C=N) + ν(C–C) 1531s, 1516s; ν(C–N) 1084m, 1029m, 951m; ν(C=S) 832s. ^{1}H NMR (δ, ppm; d-$CHCl_3$): 10.15 (s, 1H, $-N^2H$), 8.03 (s, 1H, $-C^2H$), 7.81 (m, 2H, $C^{4,8}H$), 7.68 (b, 1H, N^1H), 7.43 (m, 2H, $C^{5-7}H$), 3.30 (d, 3H, CH_3). ^{13}C NMR (δ, ppm; d-$CHCl_3$): 177.36 (C^1), 143.64 (C^2), 133.64 (C^3), 130.53 (C^6), 128.66 ($C^{4,8}$), 127.10 ($C^{5,7}$), 31.99 (CH_3).

2.1.2. Synthesis of $[Au(\kappa^1\text{-}S\text{-}HL^2)_2]Cl$ (**2**)

Gold(I) chloride (0.025 g, 0.107 mmol) was suspended in 15 mL of acetonitrile, the thio-ligand HL^2 (0.044 g, 0.214 mmol) was added and the reaction mixture was stirred for 1 h. The light yellow solution that formed was filtered and kept for crystallization. Slow evaporation at room temperature yielded crystals of $[Au(\kappa^1\text{-}S\text{-}HL^2)_2]$ Cl (**2**) (0.045 g, 65%; mp 196–198 °C). *Anal.* Calc.

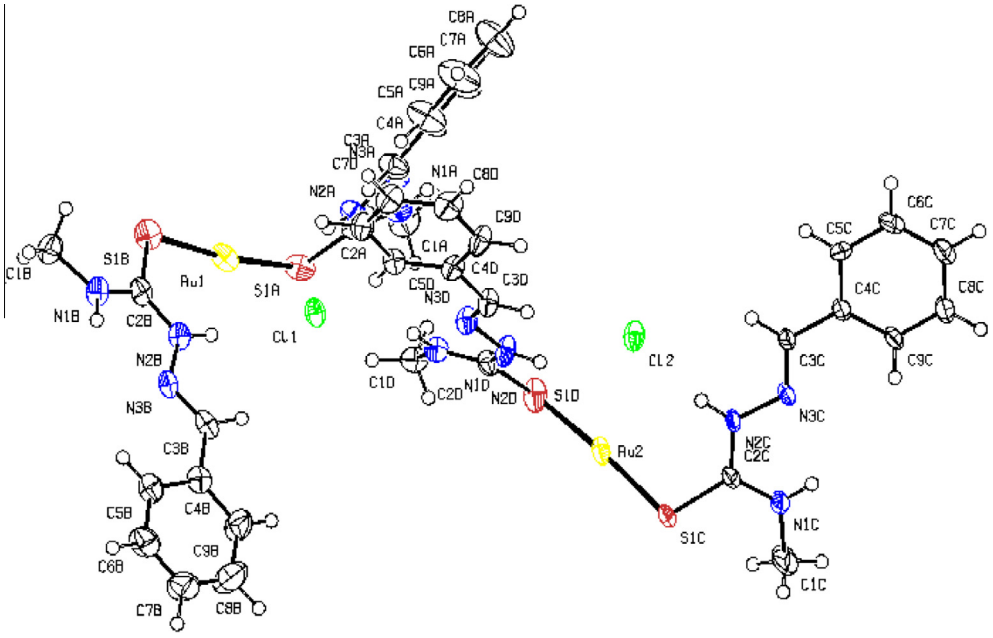

Fig. 1. Molecular structure of $[Au(\kappa^1\text{-}S\text{-}HL^1)_2]\cdot Cl$ (**1**) with the numbering scheme.

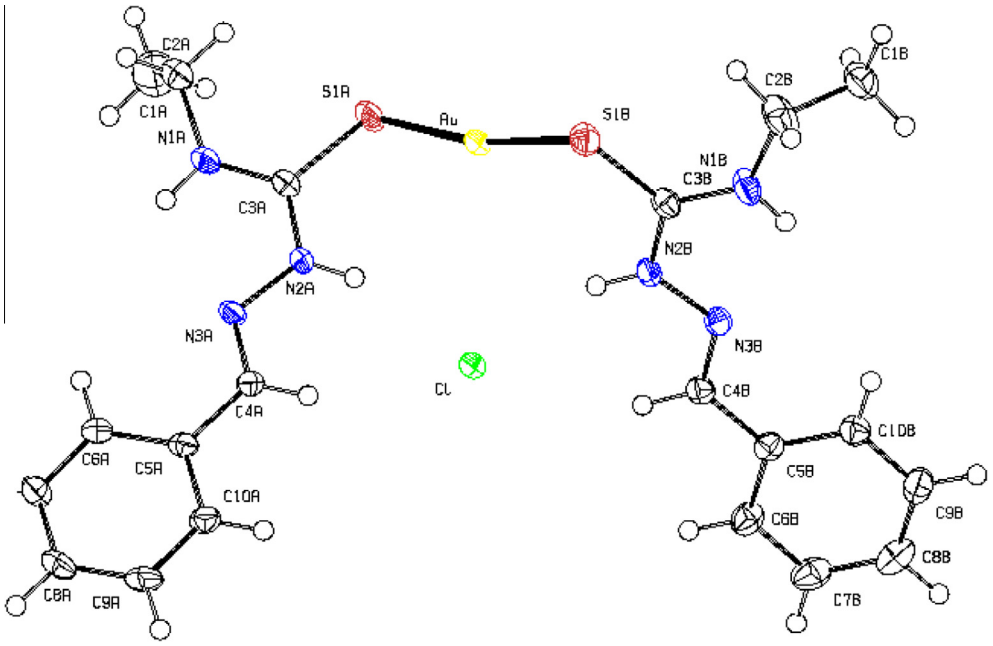

Fig. 2. Molecular structure of $[Au(\kappa^1\text{-}S\text{-}HL^2)_2]\cdot Cl$ (**2**) with the numbering scheme.

for $C_{20}H_{26}N_6S_2AuCl$: C, 37.12; H, 4.02; N, 12.99. Found: C, 37.26; H, 4.13; N, 12.76%. Main IR bands (KBr, cm^{-1}): $\nu(N^1–H)$ 3350m, 3243m; $\nu(N^2–H)$ 3100m; ν(C–H) 3061br, 2955m, 2920m; ν(C=N) + ν(C–C) 1536s, 1521s; ν(C–N) 1076m, 1029m, 954m; ν(C=S) 822s. ^{1}H NMR (δ, ppm; d-$CHCl_3$): 9.74 (s, 2H, $–N^2H$), 7.93 (s, 2H, $–C^2H$), 7.67 (m, 4H, $C^{4,8}H$), 7.47 (b, 1H, N^1H), 7.43 (m, 2H, $C^{5–7}H$), 3.80 (m, 2H, $CH_2–$), 1.35 (t, 3H, CH_3). ^{13}C NMR (δ, ppm; d-$CHCl_3$): 177.95 (C^1), 143.34 (C^2), 133.06 (C^3), 130.83 (C^6), 128.96 ($C^{4,8}$), 127.76 ($C^{5,7}$), 39.72 (CH_2), 14.27 (CH_3).

2.2. X-ray data collection, structure solution and refinement

Prismatic crystals of complexes **1** and **2** were mounted on a Gonimeter Xcalibur diffractometer equipped with a graphite

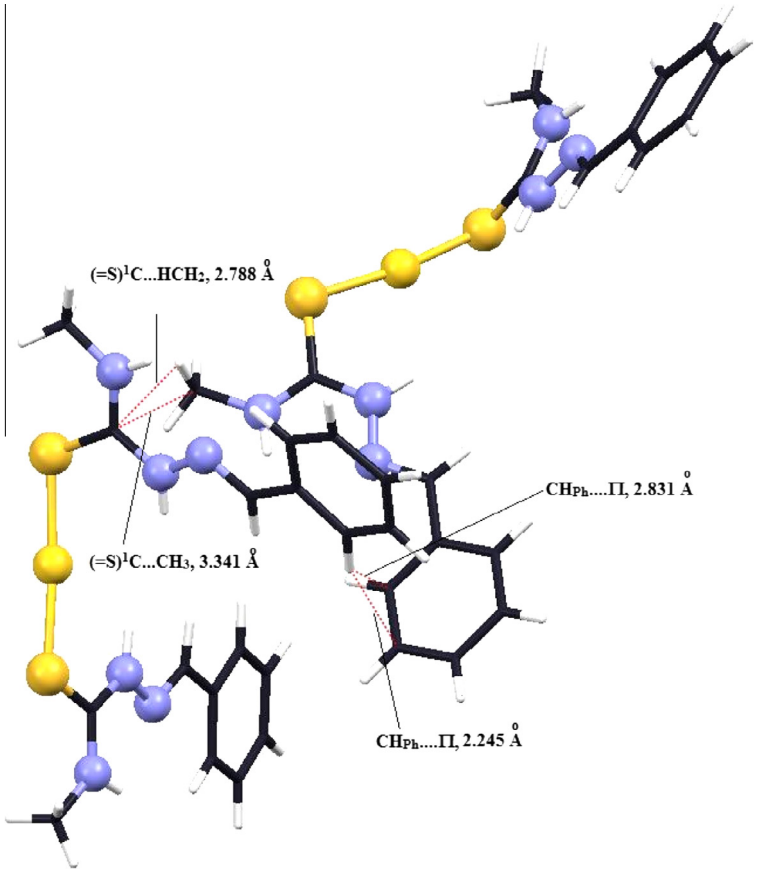

Fig. 3. Interactions between twin molecules of complex **1**.

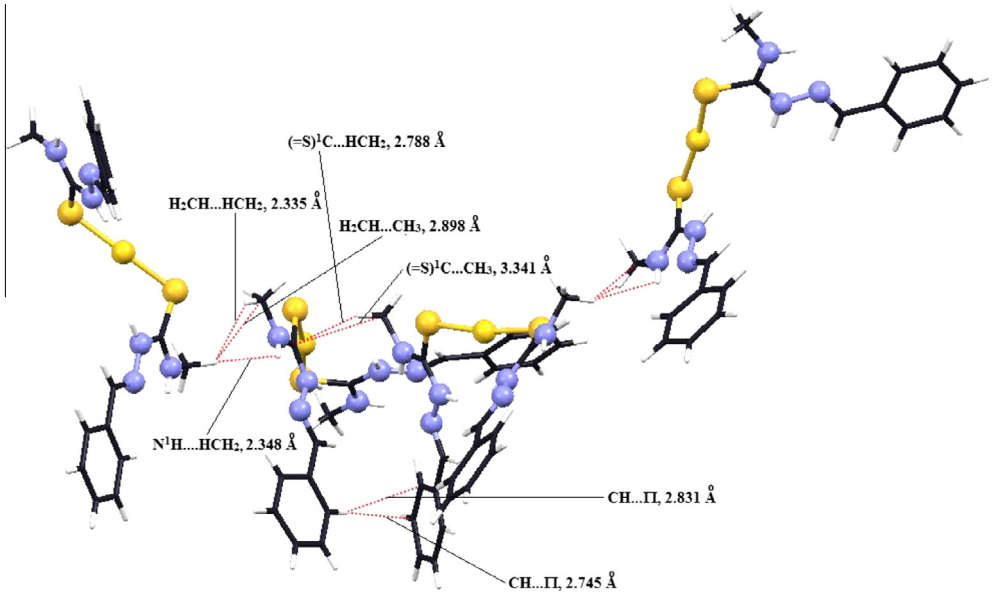

Fig. 4. Interactions between two sets of twin molecules of complex **1**.

monochromator and Mo Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 110 K. The structures were solved by direct methods and refined by full matrix least squares based on F^2 using SHELXLS-97 [27]. Structure refinement has been done using SHELXL-97 [28]. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ was used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R* factors based on all data will be even larger.

3. Results and discussion

3.1. Synthesis and IR spectroscopy of the complexes

Direct reaction of gold(I) chloride with benzaldehyde-N-methyl thiosemicarbazone (HL^1) in a 1:2 M ratio (M:L) in acetonitrile has yielded an ionic complex of the stoichiometry, $[Au(\kappa^1\text{-}S\text{-}HL^1)_2]Cl$ (**1**). Similarly, benzaldehyde-N-ethyl-thiosemicarbazone (HL^2) has also formed a similar ionic complex, $[Au(\kappa^1\text{-}S\text{-}HL^2)_2]Cl$ (**2**) (Chart 2). It is added here that earlier in the direct reaction of gold(I) chloride with 3-nitrobenzaldehyde thiosemicarbazone (Chart 1, R^1 = 3-NO_2-

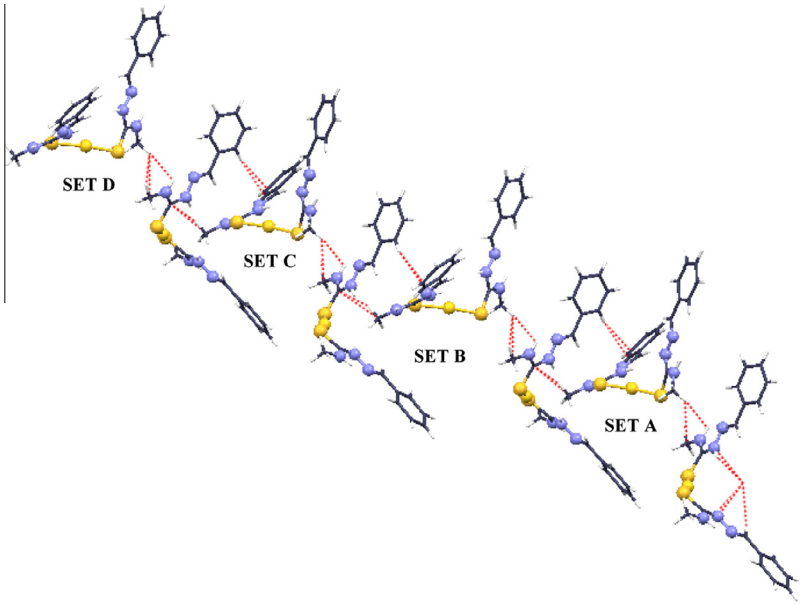

Fig. 5. Interaction between different sets of twin molecules to form a zig–zag 1D chain.

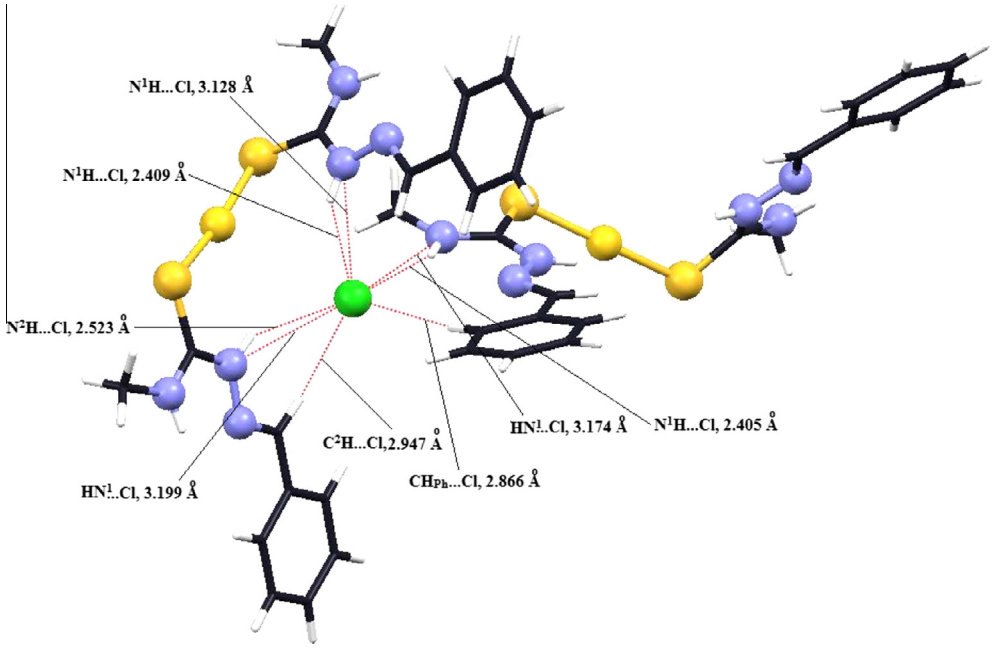

Fig. 6. Interaction of chloride ions with different hydrogen atoms in complex **1**.

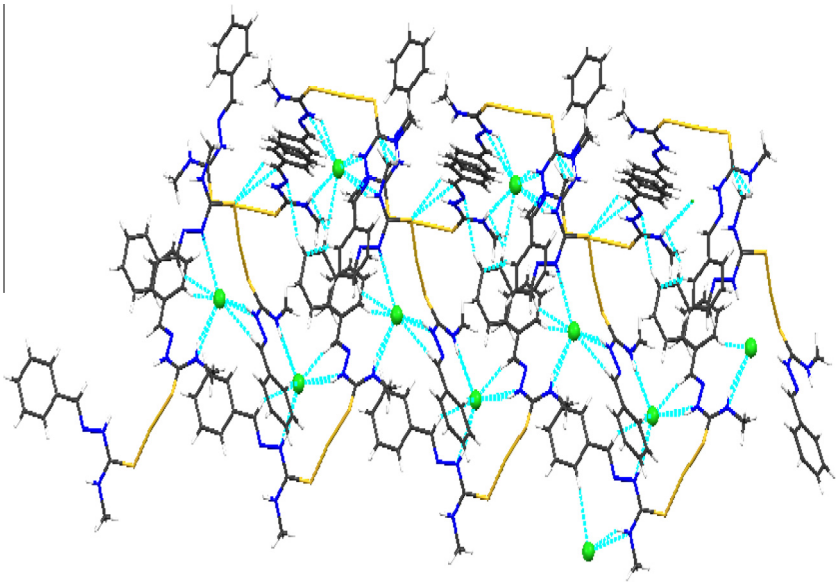

Fig. 7. Interlinking of two zig–zag chains to form the 2D sheet of complex **1**.

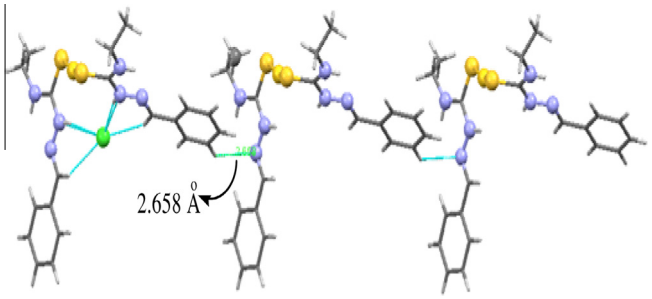

Fig. 8. The $N^{2}\cdots H–C_{Ph}$ interaction in complex **2**.

C_6H_4-; HL^3), an ionic complex $[Au(\kappa^1\text{-}S\text{-}HL^3)_2]Cl$ (**3**) was reported by this laboratory, but the presence of triphenyl phosphine was necessary to obtain a crystalline product [9]. However, the benzaldehyde thiosemicarbazone with two hydrogen atoms at the N^1 atom ($–N^1H_2$) did not yield a crystalline product, even in the presence of triphenyl phosphine, despite using a variety of solvent combinations [9]. The formation of complexes **1** and **2** in the present investigation strongly supports the role of the substituents (methyl, ethyl) at N^1 in the formation of ionic complexes, rendering the presence of triphenyl phosphine unnecessary, unlike the formation of complex **3** [9]. The gold(I) ionic complexes **1** and **2** represent the first examples obtained by the direct reaction of gold(I) chloride with a thio-ligand without the presence of PPh_3 [9] or the use of any intermediate substrate [12,14]. The IR spectral bands shown by complexes **1** and **2** are listed in the experimental section. In complex **1**, the bands due to $\nu(N^1–H)$ at 3371 and 3273 cm^{-1} and $\nu(–N^2H–)$ at 3122 cm^{-1} suggest that the thio-ligand HL^1 is coordinating to the gold metal center as a neutral ligand. The diagnostic $\nu(C{=}S)$ bands in the complexes appear at 832 and 822 cm^{-1} in complexes **1** and **2** respectively which are at lower energy relative the free thio-ligands (See ESI).

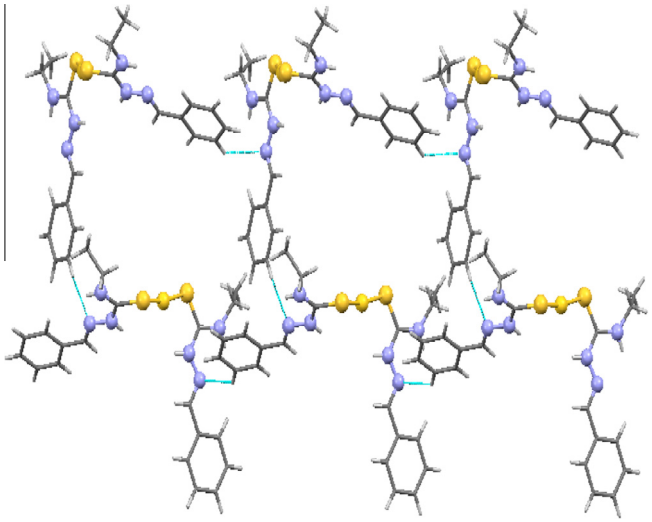

Fig. 9. Interactions between chains (via $N^{2}\cdots H–C_{Ph}$ interactions) in complex **2**.

3.2. Molecular structures

The crystallographic data of complexes **1** and **2** are given in Table 1, while important bond parameters are placed in Table 2. The molecular structures, along with numbering scheme, are given

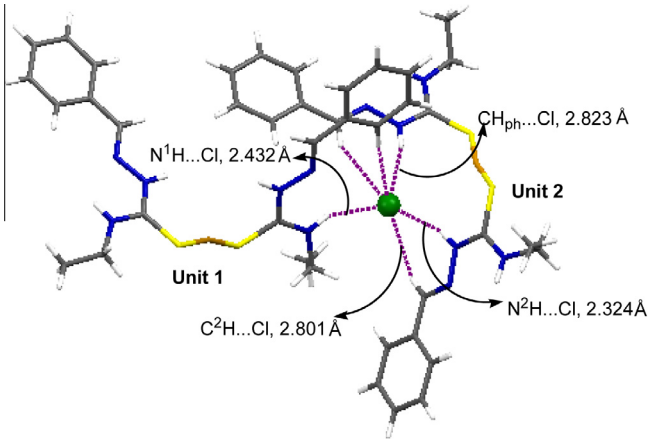

Fig. 10. Interactions of the chloride ion of complex **2**.

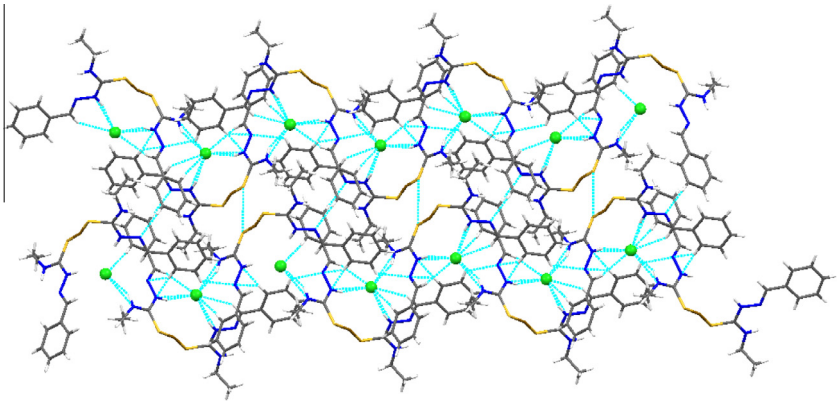

Fig. 11. Packing diagram of complex **2**.

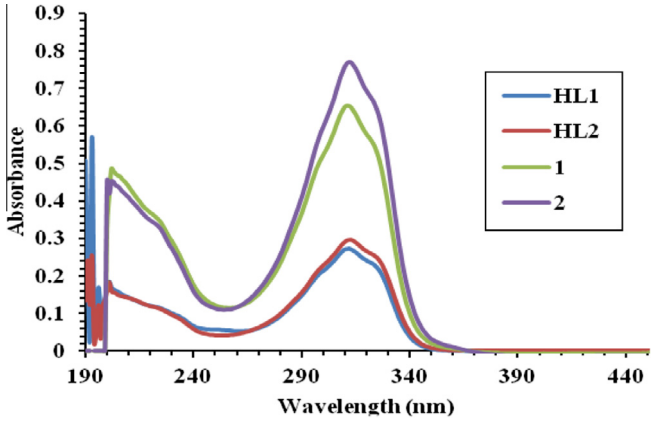

Fig. 12. Electronic absorption spectra of complexes **1** and **2** along with the spectra of the ligands (HL^1 and HL^2).

in Figs. 1 and 2 respectively. Both complexes crystallized in the monoclinic crystal system with the space group $P2_1/n$. In complexes **1** and **2**, two thiosemicarbazone moieties bind to the gold center via the thione sulfur to form a $[S\text{-}Au\text{-}S]^+$ core. For complex **1**, two molecules crystallized in the asymmetric unit, which interact with one another, and the bond parameters of these molecules are slightly different from each other (Fig. 1 and Table 2). The Au–S bond distances are Au(1)–S(1B) 2.2760(14), Au(1)–S(1A) 2.2839(14), Au(2)–S(1D) 2.2686(15) and Au(2)–S(1C) 2.2717(16) Å. These Au–S distances are comparable to those found in the literature [9,12,14]. The Au–S bond distances are smaller than the sum of the covalent radii of Au and S, 2.36 Å [29,30]. The C–S bond lengths in **1** {1.729(6), 1.722(5); 1.727(5), 1.731(5) Å} are comparable to those reported in the literature [9,12,14]. The S–Au–S bond angles in complex **1** are 171.80(5) and 170.95(6)°, which indicate distortion from linearity. The Au–S–C bond angles of **1** are in the range 104.87(17)–109.57(18)° and are similar to literature reports [9,12,14]. The Au–S {Au–S(1A) 2.2822(6) and Au–S(1B) 2.2828(6) Å} and C–S {1.727(2) and 1.730(2) Å} bond distances in **2** are also comparable to those found in the literature [9,12,14]. The S–Au–S bond angle is more distorted in complex **2** (168.33(2)°) than in **1** due to the bulkier ethyl group at N^1 atom in **2**.

3.3. H-bonded polymeric networks

In order to understand how complex **1**, with a methyl substituent at the N^1 atom, has two independent molecules in the unit cell unlike only one molecule in case of complex **2**, hydrogen bonding and other interactions are discussed in a stepwise fashion (Figs. 3–7). The hydrogen atoms of the methyl group at the N^1 atom of the thiosemicarbazone ligand of one molecule showed an interaction with the thione carbon atom of the second molecule (Fig. 3). In addition, there are $C\text{–}H_{(Ph)}\cdots\pi_{(Ph)}$ interactions between the two molecules (2.745 and 2.831 Å). These interactions appear to be responsible for the formation of two molecules. Fig. 4 shows the interaction between two sets of independent molecules wherein the methyl group of one set has agostic interactions with

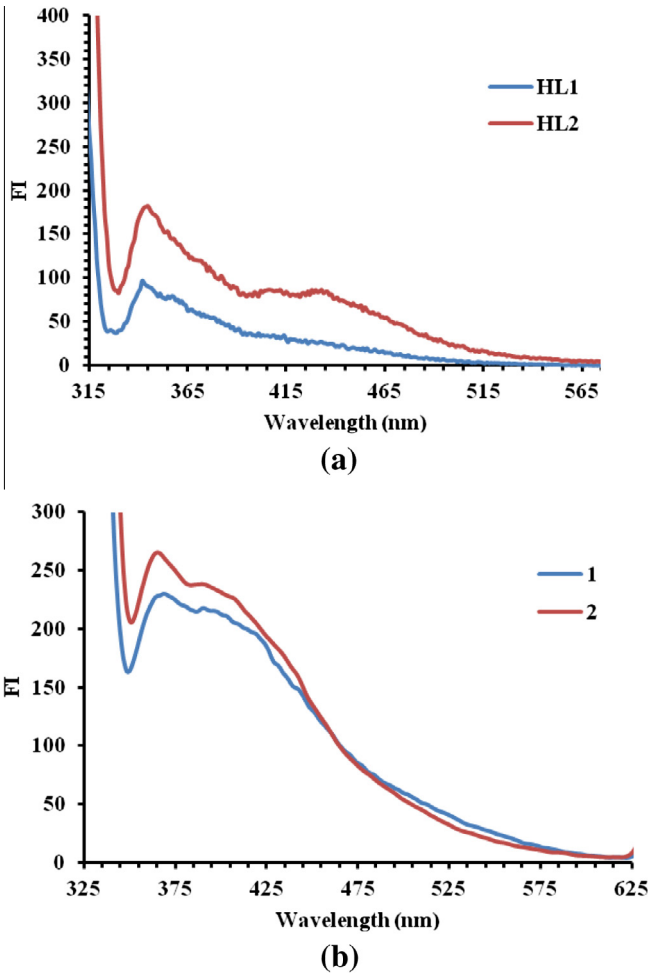

Fig. 13. (a) Fluorescence spectra of the ligands HL^1 and HL^2; (b) fluorescence spectra of complexes **1** and **2**.

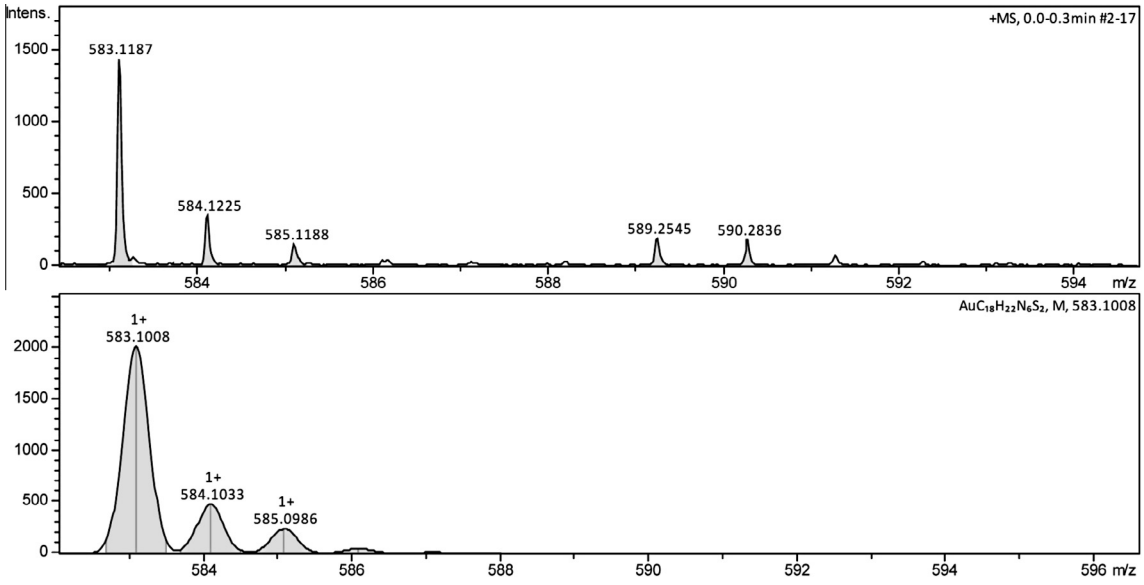

Fig. 14. ESI mass peaks for $[Au^{I}(HL^{1})_2]^+$ (**C**) (m/z = 583.11 obsd; 583.10 calcd.).

the methyl group of the second set (C–H···σ electrons interact with the C–H hydrogen atoms of the second set; H_2C–H···HCH_2, 2.335 Å and H_2C–H···CH_3, 2.898 Å) and its N^1–H moiety (N^1H···HCH_2, 2.348 Å). These types of interactions continue to form a zig–zag 1D chain (Fig. 5). Various interactions of the chloride ion are shown in Fig. 6. Two zig–zag chains are inter-linked via H_2C–H···CH_3 (2.898 Å), H_3C···CH_3 (3.602 Å) and N^1H···HCH_2 (2.348 Å) interactions, along with chloride interactions, to form a sheet-like structure (Fig. 7).

The interactions are different in complex **2**. Here the N^2 atom of one of the thiosemicarbazone ligands of one molecule shows a weak interaction with the phenyl ring of a thiosemicarbazone ligand of a second molecule, N^2···HC_{ph} 2.658 Å. These interactions are repeated to form a 1D chain (Fig. 8). The N^2 atom of this molecule also shows a similar interaction with the phenyl ring of a thiosemicarbazone ligand of second chain to form 2D sheet-like structure (Fig. 9). The interactions of the chloride ion are shown in Fig. 10. Finally Fig. 11 represents the combined packing, which includes various interactions. It is added here that in complex **2** the ethyl group does not show any type of interaction, unlike complex **1** wherein the methyl group at the N^1 atom appears instrumental in forming a pair of two independent molecules with different intermolecular interactions.

3.4. NMR (^{1}H and ^{13}C), electronic absorption and fluorescence spectroscopy

The ^{1}H NMR spectrum of complex **1** shows an –N^2H proton signal at 10.15 ppm and likewise complex **2** shows this signal at 9.74 ppm, which are at lower fields relative to the free ligands (HL^1, 9.81 ppm; HL^2, 9.50 ppm). This strongly supports that both the thio-ligands coordinate to the metal center as neutral ligands in their complexes. Various other proton signals due to –C^2H, phenyl ring protons, methyl and ethyl protons are either marginally low field or are unaffected. The ^{13}C NMR spectra of complexes **1** and **2** show signals due to C^1, C^2, phenyl ring carbons, methyl and ethyl carbons. The C^1 carbons are upfield, C^2 carbons low field and the others are minimally affected (see experimental section and ESI*).

The electronic absorption spectra of 10^{-5}M solutions of the ligands and complexes in methanol are shown in Fig. 12. Complex **1** shows one absorption band at λ_{max} = 308 nm ($\varepsilon = 6.02 \times 10^4$ L M^{-1} cm^{-1}), while complex **2** also shows one band at λ_{max} = 312 nm ($\varepsilon = 7.70 \times 10^4$ L M^{-1} cm^{-1}). The ligands also show absorption maxima at 307 nm ($\varepsilon = 2.71 \times 10^4$ L M^{-1} cm^{-1}, HL^1) and 311 nm ($\varepsilon = 2.97 \times 10^4$ L M^{-1} cm^{-1}, HL^2). These electronic absorption bands are assigned to $n, \pi \rightarrow \pi^*$ transitions. It can be noted that complexation has enhanced the molar absorptivity by a factor of more than two, though the band positions are essentially unchanged. The solutions of the ligands in methanol show weak emissions in the region 315–520 nm (maximum FI = 95 **HL^1** at λ = 343 nm, 180 **HL^2** at λ = 344 nm) (λ^{ex} = 308 nm), while both complexes show intense fluorescence bands in the wide region 325–625 nm (maximum FI = 230 **1** at λ = 367 nm, 270 **2** at λ = 365 nm) (λ^{ex} = 308 nm) (Fig. 13). The interaction of the ligands with gold(I) ions has significantly enhanced the fluorescence intensity and thus the origin of the fluorescence appears to be based on the thio-ligands (Fig. 13).

3.5. ESI-mass studies

ESI-mass spectral data for both complexes have been obtained. Complex **1** showed three lines at m/z values of 231.1, 461.2 and 583.1, which suggest the species as $[Au^{I}Cl+H]^+$ (**A**) (calcd. m/z = 232.9), $[Au^{I}Cl_2(HL^1)+2H]^+$ (**B**) (calcd. m/z = 461.9) and $[Au^{I}(HL^1)_2]^+$ (**C**) (calcd. m/z = 583.1). Complex **2** showed one signal at m/z = 607.1, corresponding to the species $[Au^{I}(HL^2)_2\text{-}4H]^+$ (**D**) (calcd. m/z = 607.1). For complex **1**, species **C** is in conformity with the solid state molecular structure (Fig. 14). It also shows species **A**, with no thio-ligand coordinated, and species **B**, which shows that gold is bonded to a neutral thio-ligand and two halogen atoms. With regards to complex **2**, only one species, **D**, was identified (see supplementary for more details of ESI-mass with isotopic patterns).

4. Conclusion

From this study it is concluded that the use of suitable thio-ligands, namely HL^1 and HL^2, have made it possible to prepare gold(I) ionic complexes **1** and **2** by the direct reaction of a metal salt with the thiosemicarbazone ligand. It is important to know that benzaldehyde thiosemicarbazone, with two hydrogen atoms at the N^1 atom (–N^1H_2), did not yield a crystalline product, even in the presence of triphenyl phosphine, despite using a variety of

solvent combinations [9]. The formation of complexes **1** and **2** in the present investigation strongly supports the role of the substituents (methyl and ethyl in the present case) at the N^1 atom in the formation of ionic complexes, rendering the presence of triphenyl phosphine unnecessary, unlike the formation of complex **3** [9]. Complex **1**, with a methyl substituent at the N^1 atom, has two independent molecules in the crystal lattice, while complex **2**, with an N-ethyl substituent, has only one type of molecule in the crystal lattice. Both complexes have shown intense fluorescence bands in the wide region 340–540 nm corresponding to an excitation wavelength of 308 nm. The synthesis of gold(I) ionic complexes might be useful from a bio-chemical point view as such complexes do not have PPh_3 bonded molecules.

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Appendix A. Supplementary data

CCDC 1017811 and 1017812 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.01.029.

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