Thiosemicarbazones of silver(I): Synthesis, spectroscopy and reactivity towards triphenylphosphine

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The new tripodal ligand tris-[2-benzaldehyde]-o xoethy]amine-thiosemicarbazone, \( \text{NCH}_2\text{CH}_2\text{O}-(\sigma\text{-C}_6\text{H}_4\text{CH=N-NH-C(=S)-NH}_2) \) (abbreviated as H1) on reaction with silver(I) acetate in 3:1 (M:L) mol ratio in ethanol forms \( \{\text{Ag}_2\text{L(OAc)}_2\} \) (1), which in presence of excess triphenylphosphine \( (\text{PPh}_3) \) in chloroform-ethanol mixture yield, \( \{\text{AgL(PPh}_3\text{)}\}_2 \)) (2). Similarly, reactions of silver(I) acetate with salicylaldehyde thiosemicarbazone \( (\text{HL}) \) and pyrrole-2-carbaldehyde thiosemicarbazone \( (\text{Hpts}) \) and pyrrole-2-carbaldehyde thiosemicarbazone \( (\text{Hpts}) \) in presence of \( \text{PPh}_3 \) in ethanol-chloroform form \( \{\text{AgL(PPh}_3\text{)}\}_2 \) complexes \( (3-5) \). The complexes \( (1-5) \) have been characterised by their physical properties, analytical data, IR and UV spectroscopic studies.

Theoismicarbazones contain chemically active, \( =\text{N}^2=\text{N}^3\) (H)-C(=S)-group and exist in E-mode (Ia) in the neutral form which changes to Z-mode (Ib) after its deprotonation and subsequent coordination to a metal centre. Thiosemicarbazones usually bind to a metal via S (monodentate) or N3, S-bidentate donor atoms; however, if the organic groups attached to C2 contain coordinating groups like pyridyl, the thiosemi-carbazones bind to the metal via N4, N5, S-donor atoms.

The interest in coordination chemistry of thiosemicarbazones is on account of the following reasons: (a) metal-thiosemicarbazone interactions offer a variety of bonding properties and structural novelties, (b) metal-derivatives of thiosemicarbazones display better pharmacological properties over thiosemicarbazones, and (c) thiosemicarbazones are biodegradable and thus provide further impetus to study metal-thiosemicarbazone interactions by varying both the components. It is observed that transition metal-thiosemicarbazone interactions have been more intensively investigated vi-s-a-vis that with the main group elements due to greater role of former metals in pharmacology.

In view of our interest in metal-thiosemicarbazone interactions, recently a series of organomercury(II) thiosemicarbazonates \( (\text{RHg}^2) \), \( R=\text{C}_6\text{H}_5-, 2-\text{C}_6\text{H}_4\text{NC}_6\text{H}_5-, \) have been reported by our group. In this paper, we report, (i) the synthesis of a first tripodal tris(thiosemicarbazone) \( III \), study its coordination behaviour with silver(I) and (ii) the mixed-ligand silver(I) complexes containing thiosemicarbazones \( \{\text{HL: R=N}^3=\text{N}^2\text{H}-\text{C}(=\text{S})-\text{NH}_2, \text{R=IV-VI}\} \) and triphenylphosphine. To our knowledge, there is one report describing mixed-ligand complexes containing \( d^10 \) metal-tertiary phosphines-thiosemicarbazones.

**Experimental**

Tris(2-chloroethyl)amine \( [(2-\text{Cl-CH}_2\text{-CH}_2)\text{N}] \) was prepared by the literature method by initially converting triethanolamine \( [(2-\text{HO-CH}_2\text{-CH}_2)\text{N}] \) to its hydrochloride by reacting it with conc. hydrochloric acid and subsequently treating it with pure thionyl chloride \( (\text{SOCl}_2) \). All the chemicals as mentioned above as well as salicylaldehyde, furan-2-carbaldehyde, pyrrole-2-carbaldehyde, thiosemicarbazide, triphenylphosphine and silver(I) acetate were procured from standard firms and generally used as such.
The C, H and N elemental analyses were obtained with a Carlo-Erba 1108 microanalyser from the University of Santiago, Spain. The melting point was determined with a Gallenkamp electrically heated apparatus. IR spectra were recorded using KBr pellets on FT-IR-NICOLET 320 Fourier Transform Spectrophotometer in the 4000-500 cm⁻¹ range. The UV spectra of the compounds were recorded on a Shimadzu UV-visible Recording spectrophotometer UV-240. The ¹H and ¹³C spectra of the compounds were recorded using Bruker AC 200 at 200MHz (for proton NMR) and at 50MHz (for ¹³C NMR). The solvent used was CDCl₃ with TMS as the internal reference.

Preparation of tripodal tris(thiosemicarbazone), N(CH₂-CH₂-O-(o-C₆H₄-CHO))₃-amine

To a solution of salicylaldehyde (4.85g, 0.04 mol) in 200 ml of ethanol was added powdered sodium hydroxide (2.12 g, 0.016 mol) followed by refluxing for 15 min and then solid tris(2-chloroethyl)amine (3.2 g) was added and the contents refluxed for half an hour. The solution was filtered and left at room temperature to crystallise for 5-6 h and the brown colored crystals of tris-[2-benzaldehyde]-oxoethyl-amine [N(CH₂-CH₂-O-(o-C₆H₄-CHO)]₃ formed were filtered, washed with water, ethanol and finally with chloroform. M.pt. 87°C, yield, 75 %. To a solution of thiosemicarbazid (0.60 g, 6.593 mmol) in 40 ml of hot water was added slowly a solution of tris-[2-benzaldehyde]-oxoethylamine (1.20 g, 2.603 mmol) in 75ml of ethanol. The mixture was refluxed for 5-6 h and the light yellow solid formed was filtered after cooling the contents, washed with chloroform and dried in vacuo. Yield 80%, m.pt. 158-60°C. It is soluble in DMSO, DMF, significantly soluble in ethanol and poorly soluble in chloroform. Analytical data [Found, C, 52.66; H, 6.13; N, 18.08; Required for C₉H₉N₂O₂S₃, C, 52.85, H, 6.22, N, 18.13%]. IR data: 3400w, 3175w (VNC=O); 3050w, 2975m, 2850w (VC=O); 1655w (δCH₂); 1598s (VC=S); 1451s (VC=N); 1483s, 1446s, 1362s (VNC + δCH₂); 1250s, 1160s, 1125m (VNC + VC=S, N-CH₂-CH₂-O-group); 1043s, 817s (VC=S); 754s (ring breathing mode). NMR data (δ, ppm): H, 11.12, 10.42, (N₂H); 8.39 (CH₃), 7.31 (CH₃ + NH₂); 6.92 (CH₃, C=), 4.69 (OCH₃), 2.59 (NCH₂); 136.8, 130.9, C, 125.6, C, 122.0, C, 120.3, C, 112.1, C, 67.3 C, 53.6, C.

Other thiosemicarbazones, namely, salicylaldehyde thiosemicarbazone (H₂tsc), furan-2-carbaldheyde thiosemicarbazone (H₂tsc) and pyrrole-2-carbaldheyde thiosemicarbazone (H₂tsc) were prepared as reported in literature.

Preparation of complexes

[AgsL(OAc)₂] (1)

To a solution of silver(I) acetate (0.075 g, 0.450 mmol) in 30 ml of ethanol was added a solution of tris(thiosemicarbazone) [H₃L, 0.100 g, 0.150 mmol] in 40 ml of ethanol. The contents were stirred for overnight and the light brown solid formed was filtered, washed with ethanol and chloroform and dried in vacuo. Yield, 60%; m.pt. 108-110°C. It is sparingly soluble in ethanol, acetonitrile, benzene, and chloroform. Analytical data: [Found, C, 29.3, H, 2.91, N, 11.70; Required for C₅H₅N₂O₂S₃Ag (30.7, H, 2.92, N, 10.50%). IR data: 3400w, (νVC=O); 2764w (νVC=O); 1660w (δC=O); 1599s (VC=S); 1511w (νVC=O); 1485s, 1450s, 1384s (νVC + δC=O); 1290s, 1243a, 1162s (νVC + νC=O, N-CH₂-CH₂-O-group); 1042 m, 805 m (νVC=S); 755s (ring breathing mode).

[AgsL(OAc)₂(PPh₃)₂] (2)

To a solution of silver(I) acetate (0.075 g, 0.450 mmol) in 30 ml of ethanol was added a solution of tris(thiosemicarbazone) [H₃L, 0.100 g, 0.150 mmol] in 40 ml of ethanol. The contents were stirred for 5-6 h when a light brown solid was formed and to this mixture was added a solution of triphenylphosphine (0.235g, 0.900 mmol) in 30 ml chloroform and stirring continued for about an hour until a clear solution was formed. The solution was filtered and a light yellow solid was obtained on slow evaporation. Yield, 58%; m.pt. 168-70°C. It is soluble in common organic solvents such as ethanol, acetonitrile, benzene, chloroform etc., Analytical data: [Found, C, 67.9, H, 4.94, N, 3.12; Required for C₃₂H₃₆N₆O₆S₃P₂Ag₃, C, 67.0, H, 4.90, N, 3.12%]. IR data: 3050w, 2670w (νVC=O); 1670w (δC=O); 1598w (νVC=S); 1528w (νVC=S); 1478s, 1343m, 1339s, 1323s, 1290 w (υVC + δC=O); 1250 m, 1157s, 1163s (υVC + μC=O, N-CH₂-CH₂-O-group); 1090s (υC=S). 1025w, 820v (υC=S); 750m (ring breathing mode).

[AgsL(OAc)₂(PPh₃)₂].2H₂O (3)

To a solution of silver(I) acetate (0.050 g, 0.300 mmol) in 15 ml of water-ethanol mixture (a few drops of water needed) was added a solution of H₂tsc (0.060 g, 0.300 mmol) in 10 ml of ethanol. The contents were stirred for 3 h when a white turbid mixture was formed and to this mixture was added a
solution of triphenylphosphine (0.117 g, 0.500 mmol) in 10 mL chloroform and stirring continued for further 2 h until a clear solution was formed. The mixture was filtered and white solid was obtained on slow evaporation. Yield, 67%; m.p. 188-90°C. It is soluble in warm ethanol, acetonitrile, benzene or chloroform.

Analytical data: [Found, C, 51.0, H, 3.83, N, 7.3; Required for C35H27N3PSO, Ag C, 52.0, H, 4.50, N, 7.0%]. IR data (cm⁻¹): 3420w (νO-H), 3290w, 3146w (νN-H); 1603m (δN-H); 1541s (νC=N); 1095s (νP-C), 823m (νC=S); 741s, 692s (ring breathing mode). [IR peaks for free Hpnps: 3444s (νO-H), 3216s, 3172m (νN-H)].

It is soluble in common organic solvents such as ethanol, acetonitrile, benzene or chloroform. Analytical data: [Found, C, 65.7, H, 4.71, N, 3.64; Required for C35H27N3PSO, Ag C, 64.7, H, 4.59, N, 3.74%]. IR data (cm⁻¹): 3385w, 3256w, 3129w (νN-H); 1604m (δN-H); 1541m (νC=N); 1095s (νP-C), 1060w, 823m, (νC=S); 743s, 692s (ring breathing mode). [IR peaks for free Hfnps: 3405s, 3291s, 3120m (νN-H), 1615s (δN-H), 1578s (νC=N); 1060s, 841s (νC=S); 779s, 757s (ring breathing mode)].

Compounds (4) and (5) were prepared similarly. [Ag(Hfnps)(PPH₃)₄]0.5CHCl₃ (4)

(1:1 mol ratio was used). Yield, 71%; m.p. 90-92°C. It is soluble in common organic solvents such as ethanol, acetonitrile, benzene or chloroform. Analytical data: [Found, C, 65.7, H, 4.71, N, 3.64; Required for C35H27N3PSO, Ag C, 64.7, H, 4.59, N, 3.74%]. IR data (cm⁻¹): 3385w, 3256w, 3129w (νN-H); 1604m (δN-H); 1541m (νC=N); 1095s (νP-C), 1060w, 823m, (νC=S); 743s, 692s (ring breathing mode). [IR peaks for free Hfnps: 3405s, 3291s, 3120m (νN-H), 1615s (δN-H), 1578s (νC=N); 1060s, 841s (νC=S); 779s, 757s (ring breathing mode)].

[Ag(hfnps)(PPH₃)₄] CHCl₃ (5)

(1:1:2.54: Ag: psc: PPH₃ mol ratio used). Yield, 74%; m.p. 130-32°C. It is soluble in common organic solvents such as ethanol, acetonitrile, benzene or chloroform. Analytical data: [Found, C, 65.8, H, 4.65, N, 3.30; Required for C35H27N3PSO, Ag C, 65.7, H, 4.71, N, 3.88%]. IR data (cm⁻¹): 3470w, 3251w, 3053m (νN-H); 1611m (δN-H); 1533m (νC=N); 1091s (νC=S); 828m, (νC=S); 743s, 692s (ring breathing mode). [IR peaks for free Hfnps: 3450s, 3267s, 3148s (νN-H); 1650m (δN-H), 1587s (νC=N); 1124s, 832s, (νC=S); 777s, 741s (ring breathing mode)].

**Results and discussion**

The tripodal ligand (H₅L), N[CH₂CH₂O·(o-C₆H₄-CH=N·NH·C(=S)·NH₂)]₃, was prepared by the reaction of tris-[2-benzaldehyde] oxoethyl] amine, N(CH₂CH₂O·[o-C₆H₄·CHO]₃, with thiosemicarbazide, NH₂·NH·C(=S)·NH₂ (1:3 mole ratio) in water-ethanol. The characteristic IR peaks due to various groups such as νN-H, νC-H, νC=O, νC=N, νC=S etc and ¹H and ¹³C NMR data are listed in the experimental section and are in conformity with the literature values for thiosemicarbazones. The N-H protons absorb at 11.12, 10.42 ppm indicating that this group is under two different chemical environments; however, C-H protons show a single peak at 8.39 ppm. The peaks due to NH₂ group merge with C-H protons. In the ¹³C NMR spectrum of H₅L, the C-carbon of thiosemicarbazide moiety [C(=S)NH₂] shows a signal at δ = 177.7 ppm and C₂ carbon absorbs at δ = 163.8 ppm. Other ¹³C signals are as listed in experimental section.

The tripodal ligand contains three dissociable N-H protons and on reaction with silver(I) acetate formed [Ag₅L(OCOCH₃)] (1) which on further reaction with triphenylphosphine (PPH₃) in chloroform-ethanol yielded [Ag₅L(OCOCH₃)(PPH₃)₂] (2). The IR spectra of the compounds 1-2 (cf. experimental section) are clearly different from that for the ligand and suggest formation of new compounds. In compound 1, the νC=O appears at 1551cm⁻¹ as a weak peak and this shows coordination of N₃ nitrogen with silver. Similarly, the νC-S peaks at 1041cm⁻¹ and 805cm⁻¹ are weak in intensity and support coordination via sulphur. The behaviour of compound 2 is similar as νC=O appears at 1528cm⁻¹ as a weak and shifted peak and νC-S peak at 1043 cm⁻¹ in the free ligand shifts to 1025(w) cm⁻¹.

The UV spectrum of free H₅L in chloroform shows two peaks of medium intensity at 348 and 328 nm due to n→π* transitions of C=S group while a strong peak at 256nm is assigned to absorption due to n→π* of C=N group. In the complex 2, very strong absorption occurs at 275nm with a shoulder at 250nm (n→π* transitions of C=S group ) and the peaks in the low energy region (350, 330 nm) are greatly reduced in intensity due to coordination of sulphur to metal centre. The peaks due to PhP at 218nm (π→π*) and 259nm (n→π*) get merged with n→π* transition of C₅ group of thiosemicarbazone.

With other thiosemicarbazones a series of complexes, [Ag(Hfnps)(PPH₃)] (3), [Ag(Hfnps)(PPH₃)] (4) and [Ag(hfnps)(PPH₃)] (5) were formed. In all these compounds, thiosemicarbazones are acting as uninegative anions undergoing deprotonation of N-H protons as is commonly observed in metal-thiosemicarbazone chemistry. The IR spectra of the complexes show the formation of new compounds (experimental section). The compound 3 shows νC=N at 1541s cm⁻¹ which is at lower energy as compared with the free ligand peak at 1603cm⁻¹ and it suggests coordination via N nitrogen and it is similar for the
compounds 4 and 5. The V-curves of complexes 3-5 appear at different positions and also generally involve reduction in intensity. Thus, thiosemicarbazones are coordinating as anions via N', S-donor atoms. The presence of PPh₃ is confirmed from its characteristic peak (νre) in the region 1090-1095 cm⁻¹.

The UV spectrum of free H₂stsc in ethanol shows intense peaks at 333 nm (n→π*, C=S), 305 nm (n→π*, C=N) and medium intensity peaks at 218 and 240 nm (π→π*, Ph group) and its compound 3 shows a strong peak at 215 nm (π→π*), a medium peak at 256 nm (n→π*, C=S, C=N) with absorption in the low energy almost disappeared due to blue shift. The peaks due to PPh₃ are merged with the peaks at 215 and 256 nm. The UV spectrum of Hfsc in ethanol shows a weak peak at 214 nm (π→π*), strong absorption at 319 nm (n→π*, C=N) and 330 nm (n→π*, C=S) and in its complex 4, there is a strong peak at 218 nm (π→π*) with medium intensity peaks at 250 nm (n→π*) and 329 nm (n→π*, C=S). The peaks at 218 nm and 250 nm incorporate absorption due to PhJP. Finally, the ligand Hfptsc showed absorption at 328 nm with weak absorption at 236 nm and in its complex 5, there is a strong peak at 216 nm, medium peak at 256 nm and a weak peak at 332 nm. The UV spectra of 3-5 clearly support coordination by N, S-donor atoms of thiosemicarbazones and PhJP ligand.

The structure of 3 is proposed as tetrahedral with tridentate Hstsc (via N\(^{\ddagger}\), S, OH) and monodentate PPh₃. Similarly, for 4 and 5 octahedral structures are suggested with fsc coordinating via furan oxygen O, S and N\(^{\ddagger}\) donor atoms and ptsc via S, N\(^{\ddagger}\) atoms with remaining positions occupied by PPh₃ molecules (structures VII-IX).

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References