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Silver(I) complexes of imidazolidine-2-thione and triphenylphosphines: Solid-state, solution NMR and antimicrobial activity studies

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Abstract. Mixed ligand complexes of Ag(I) with triphenylphosphine (PPh_3), triphenylphosphine sulfide ($SPPh_3$), triphenylphosphine selenide ($SePPh_3$) and Imidazolidine-2-thione (Imt) have been prepared. The solution as well as solid state NMR studies have been carried out to characterize these complexes. Both solid and solution NMR show the coordination via thione group on one side and (S/Se) or PPh_3 on the other side. A higher antimicrobial activity is shown by [ImtAgPPh_3]Cl complex against gram negative *Pseudomonas aeruginosa* (*P. aeruginosa*) and *Escherichia coli* (*E. coli*) compared to the other two complexes i.e. [ImtAg$SPPh_3$]Cl and [ImtAg$SePPh_3$]Cl.

Keywords: Silver(I) complexes, imidazolidine-2-thione, triphenylphosphines, CP MAS NMR, antimicrobial activity

1. Introduction

The complexation capacity of thiourea derivatives is well known [1–4] and the biological activities of thiourea complexes have been studied for different biological systems [5]. In recent years, the antifungal activity of thioureas and substituted thioureas and their Ni(II), Cu(II), Pt(II) and Co(III) complexes against phytopathogenic fungi and yeast have been studied [6–9]. Recent research has also shown that silver(I) is known to interact with selenium in the body resulting in a reduction of toxicity of both the metal ion and selenium [10,11]. Therefore, an investigation of silver complexation with selenium-containing ligand is important from a biological point of view.

The present report describes the solid state NMR studies of [ImtAgL]Cl (where L = PPh_3, $SPPh_3$ or $SePPh_3$) complexes by ^{1}H, ^{13}C, ^{31}P, ^{77}Se and ^{109}Ag NMR spectroscopy.

Silver complexes are known to dissociate in solution, and as such solid state NMR studies on Ag–S and Ag–Se containing complexes are studied and compare them with solution chemistry of these complexes [12].

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2. Experimental

2.1. Materials

$AgNO_3$, PPh_3, $SPPh_3$, $SePPh_3$ and DMSO-d_6 were obtained from Fluka Chemical Co. Imt was synthesized according to the procedure described in the literature by the addition of CS_2 to ethylenediammine in ether and then heating the resulting adduct at 100°C for 2–3 hrs, followed by its crystallization in methanol [13,14].

2.2. ^1H and ^{13}C NMR measurements

^{1}H NMR spectra were obtained on Jeol JNM-LA 500 NMR spectrometer operating at a frequency of 500.00 MHz. ^{13}C NMR spectra were obtained at the frequency of 125.65 MHz with ^{1}H broadband decoupling at 298 K. The spectral conditions were: 32 k data points, 0.967 s acquisition time, 1.00 or 30.00 s pulse delay and 45° pulse angle. ^{13}C chemical shifts relative to TMS were assigned according to the reference given in the literature [15].

2.3. Solid state NMR studies

Solid state cross-polarization magic-angle spinning (CPMAS) $^{31}P\{^1H\}$ NMR spectra were obtained a JEOL LAMBDA 500 spectrometer operating at 202.35 MHz (11.74 T), at ambient temperature of 25°C. Samples were packed into 6 mm zirconium oxide rotors. The magic angle spinning rates were from 2000 Hz to 5000 Hz. Contact time of 3 ms were used with a proton pulse width of 6 μs, with a recycle delay of 10 s. Approximately 500 FID's were collected and transformed with a line broadening of 50 Hz. Chemical shifts were referenced using an external sample of solid PPh_3 ($\delta = -8.40$ ppm from 85% H_3PO_4). Natural abundance ^{13}C solid state NMR spectra were obtained at ambient temperature on the same spectrometer operating at a frequency of 125.25 MHz. Cross polarization and high power decoupling were employed. Pulse delay of 7.0 s and a contact time of 5.0 ms were used in the CPMAS experiments. Carbon chemical shifts were referenced to TMS by setting the high frequency isotropic peak of solid adamantane to 38.56 ppm. CPMAS ^{77}Se spectrum was obtained on the same instrument operating at a frequency of 95.35 MHz. The contact time of 5 ms with proton pulse width of 6.0 μs, with a recycle delay of 12 s were used. Sample was spun at 3 and 5 kHz at the magic angle to determine the isotropic peak. Approximately 5000 scans were employed. ^{77}Se chemical shifts are referenced using an external ammonium selenate sample by setting its isotropic peak to 1040.2 ppm [16] relative to liquid Me_2Se at 23°C. The ^{31}P CPMAS spectra containing spinning side-band manifolds were analyzed using a program based on Maricq and Waugh [17] and developed by Durham University, UK using an iterative method.

2.4. Synthesis of [ImtAgPPh$_3$]Cl and related complexes

All three compounds were prepared in a similar manner. Typically, silver chloride (1.44 g, 1 mol) dissolved in methanol (2 to 3 cm^3) added to solution of stoichiometric quantities (1 mol) of triphenylphosphine, or triphenylphosphine sulfide, or triphenylphosphine selenide dissolved in methanol (2–3 cm^3). The suspension was reflux for 4 h and 1 mol quantities of thione (Imt) was added, reflux 5 h. The powder for each product was collected by filtration. Elemental analysis of the complexes are reported in Table 1 and the NMR chemical shifts are reported in Table 2 and Table 3 for solution and Table 4 for solid NMR respectively.

Table 1
Characterization of [ImtAgL]Cl (where L = PPh_3, $SPPh_3$ or $SePPh_3$) complexes

Complex	Found (Calcd) %				M. Pts. (°C)
	C	H	N	S	
[ImtAgPPh_3]Cl[a]	48.08 (49.67)	4.14 (4.17)	5.17 (5.52)	6.11 (6.32)	162
[ImtAg$SPPh_3$]Cl	45.84 (46.72)	4.017 (3.92)	5.19 (6.239)	11.92 (11.88)	150
[ImtAg$SePPh_3$]Cl	42.99 (43.54)	3.78 (3.61)	5.56 (4.77)	5.37 (5.47)	168

a = [24].

Table 2
^{1}H and ^{13}C NMR chemical shifts of [ImtAgL]Cl (where L = PPh_3, $SPPh_3$ or $SePPh_3$) complexes in DMSO-d_6

Species	N–H	C-2	C-4	C-5
Imt	7.98	183.44	43.97	43.97
[Imt$AgNO_3$][a]	9.04	176.96	45.14	45.14
[ImtAgPPh_3]Cl	8.84	180.31	44.52	44.52
[ImtAg$SPPh_3$]Cl	8.84	179.14	44.77	44.77
[ImtAg$SePPh_3$]Cl	8.84	179.19	44.76	44.76

a = [28].

Table 3
^{31}P and ^{107}Ag NMR chemical shifts of thiones and their [ImtAgL]Cl (where L = PPh_3, $SPPh_3$ or $SePPh_3$) complexes in DMSO-d_6

Species	^{31}P	^{107}Ag	$^{1}J(^{31}P–^{77}Se)$
PPh_3	−9.16	–	–
[AgPPh_3]Cl[a]	30.38	639.23	–
[Imt$AgNO_3$]	–	571.03[b]	–
[ImtAgPPh_3]Cl	39.20	859.65	–
[ImtAg$SPPh_3$]Cl	42.94	690.57	–
[ImtAg$SePPh_3$]Cl	35.31	631.40	$^{1}J(^{31}P–^{77}Se)$ = 360 Hz

a = [24].
b = [28].

2.5. Bioactivity

Antimicrobial activity was measured as described in the literature [18]. It was evaluated by the minimum inhibitory concentration (MIC) on three microorganisms, namely *Pseudomonas aeruginosa* (*P. aeruginosa*), Fecal Streptococcus (*FS*) and *Escherichia coli (E. coli)* and on group of organisms Heterotrotropic Plate Counts (*HPC*). *HPC* is a standardized means of determining the density of aerobic and facultative anaerobic heterotrophic bacteria in water/wastewater. It is a group of bacteria and not a single strain.

These bacteria/group of bacteria were isolated and cultured from domestic wastewater (Al-Khobar Wastewater Treatment Plant at Al-Azizia, Saudi Arabia) in which a variety of pathogens and other microorganisms present. Each analysis was carried out in duplicate to maintain the maximum accuracy. Dosage of reached a maximum dose of 1000 μg/ml was used as a stopping criterion. A stock solution of 1000 μg/ml was used to prepare consecutive dilution having concentration difference of 25 μg/ml. The [ImtAgL]Cl (where L = PPh_3, $SPPh_3$ or $SePPh_3$) complexes are insoluble in water but these bioactivities are done in water as well as in DMSO for comparison (Table 5).

Table 4
CPMAS NMR data for the complexes [ImtAgL]Cl (where L = PPh_3, $SPPh_3$ or $SePPh_3$) and the corresponding ligands[a]

Complex	Nucleus	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η
[ImtAgPPh_3]Cl	^{31}P	44.0	−108	−80	56	150	0.28
PPh_3[d]	^{31}P	−7.2					
[ImtAgPPh_3]Cl	^{13}C	167.1[b]					
[ImtAg$SPPh_3$]Cl	^{31}P	43.9	−109	−78	51	145	0.32
$SPPh_3$[d]	^{31}P		46.4				
[ImtAg$SPPh_3$]Cl	^{13}C1	63.4[b]					
[ImtAg$SePPh_3$]Cl	^{31}P	35.6	−100	−55	48	127	0.53
$SePPh_3$[e]	^{31}P	38.9	−104	−61	48		
[ImtAg$SePPh_3$]Cl	^{13}C	168.1[b]					
[ImtAg$SePPh_3$]Cl	^{77}Se	i. 251.7 (696 Hz)[c]					
		ii. 266.8 (692 Hz)[c]					
$SePPh_3$	^{77}Se	i. 242.6 (744 Hz)[c]					
		ii. 257.5 (734 Hz)[c]					

[a] Isotropic shielding, $\sigma_i = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$; $\eta = (\sigma_{22} - \sigma_{11})/\frac{2}{3}\Delta\sigma$.
[b] Thiocarbonyl carbon resonance;
[c] J_{P-Se} values; d 14; e 27.

Table 5
Antimicrobial activity for Heterotrotropic Plate Counts (*HPC*), *Pseudomonas aeruginosa* (*P. aeruginosa*) and Fecal Streptococcus (*FS*) *and Escherichia coli (E. coli)*. MIC of various ligand and their complexes are reported in (μg/ml)

Test organism	IMT (water)	IMT (DMSO)	Ag(IMT)NO_3 (water)	Ag(IMT)NO_3 (DMSO)	PPh_3 (water)	PPh_3 (DMSO)
HPC	650	650	500	475	950	950
P. aeruginosa	250	225	250	250	900	900
FS	300	300	400	350	875	850
E. coli	250	250	200	175	850	850
Test organism	PPh_3S (water)	PPh_3S (DMSO)	PPh_3Se (water)	PPh_3Se (DMSO)	AgCl (water)	AgCl (DMSO)
HPC	>1000	950	750	700	>1000	>1000
P. aeruginosa	950	925	425	400	950	900
FS	850	800	500	475	875	875
E. coli	800	800	250	250	750	700
Test organism	A in (water)	A in (DMSO)	B in (water)	B in (DMSO)	C in water	C in (DMSO)
HPC	425	425	>1000	>1000	>1000	>1000
P. aeruginosa	300	300	950	925	950	950
FS	225	200	900	900	875	850
E. coli	75	75	825	800	750	700

A = [ImtAgPPh_3]Cl; B = [ImtAg$SPPh_3$]Cl; C = [ImtAg$SePPh_3$]Cl.

3. Results and discussion

3.1. ^{1}H NMR studies

In ^{1}H NMR spectrum of the complexes, the N–H signal of thiones became less intense upon coordination and shifted downfield by 0.7–1.0 ppm from their positions in free ligands. The deshielding of N–H

proton is related to an increase of the π electron density in the C–N bond upon complexation [19]. The appearance of N–H signal shows that the ligands are coordinating to silver(I) via the thione group (see Table 2).

3.2. ^{13}C NMR studies

In all complexes, C-2 resonance appears upfield by 4–7 ppm compared to free ligands in accordance with the data observed for other complexes of Cu(I), Ag(I) and Au(I) with heterocyclic thiones [20–22]. The upfield shift is attributed to a lowering of the >C=S bond order upon coordination and a shift of N→C electron density producing partial double bond character in the C–N bond [19,23]. The upfield shift decreases as the number of ligands attached to silver(I) increases from one in [$LAgNO_3$] to two in [AgL_2]NO_3. This is because of the increase in number of electronegative groups attached to silver(I). A small shift of 1–2 ppm is observed in other carbon atoms, which shows that nitrogen atoms are not involved in coordination. The difference in shielding at C-2 is related to the strength of the metal–sulfur bond, which arises from the back donation of silver(I) to sulfur [20].

3.3. ^{31}P NMR studies

The ^{31}P NMR resonance for PPh_3 of free PPh_3 was observed at -9.16 ppm (see Table 3). After complexing with Ag(I), it shifted by 40 ppm down field. Further, down field shift is observed for $SPPh_3$ and $SePPh_3$ as trans ligands with Imt. This down field shift is due to deshielding of P-atom with extended d orbital overlap with silver(I) [24].

3.4. ^{107}Ag NMR studies

^{107}Ag NMR of $AgNO_3$ is recorded in DMSO-d_6 instead of D_2O, the signal is shifted by 166 ppm showing that the ^{107}Ag chemical shift is not only sensitive to the nature of ligands but is also affected by changing the solvent. The chemical shift of [$AgPPh_3$]Cl is 639 ppm which is shifted by about 473 ppm downfield after complexing with PPh_3 (Table 3). When the trans ligand Imt was introduced further reduction is observed. One interesting observation from this study is the effect of PPh_3, $SPPh_3$ and $SePPh_3$ on the ^{107}Ag chemical shift which increased from 859.65, 690.57 and 631.40 ppm respectively. This trend clearly indicates that PPH_3 binds more strongly to Ag(I) followed by $SPPh_3$ and $SePPh_3$. In terms of the basicity, PPh_3 is the most basic which caused the most shift from [$ImtAgNO_3$] to [$ImtAgPPh_3$]Cl. Not so significant shift was observed when $SPPh_3$ and $SePPh_3$ were complexed to Ag(I).

The very large shifts in ^{107}Ag NMR in these complexes provide a clear evidence for binding of thiones to silver (I) through sulfur atom only. The nitrogen-bonded complexes usually possess a shift of around 100 ppm in ^{107}Ag NMR [25].

3.5. Solid state NMR studies

The CP MAS ^{31}P spectrum for the complex [$ImtAgPPh_3$]Cl is shown in Fig. 1. The principal components of the chemical shift tensor were calculated from spinning side band intensities employing an iterative computer program. These are shown in Table 4 along with the chemical shift anisotropies and asymmetry parameters. The quality of the selenium spectrum was poor to reliably calculate individual chemical shift tensor values. Hence only the isotropic chemical shift values are reported in Table 4. The

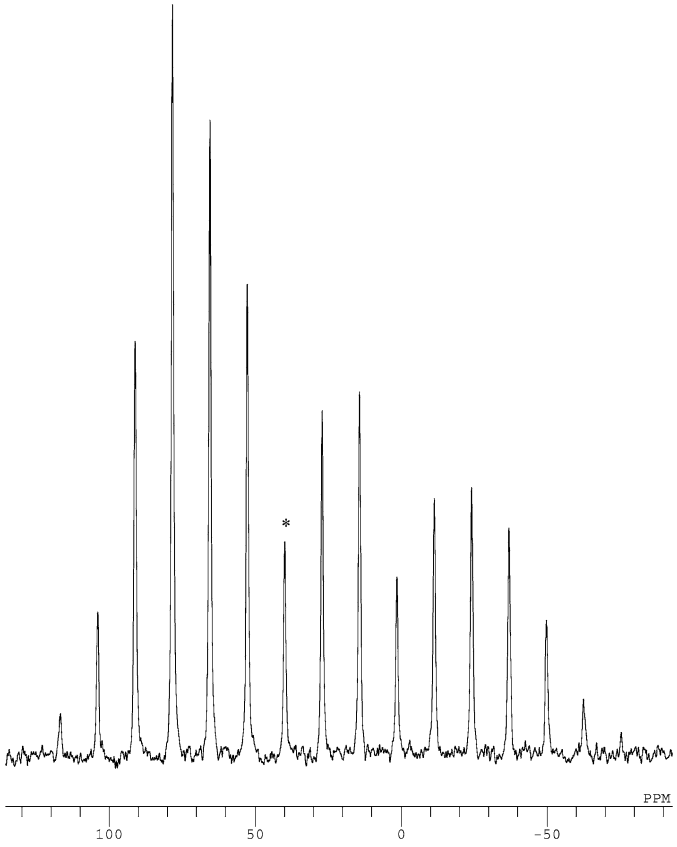

Fig. 1. ^{31}P CPMAS NMR spectrum of [ImtAgPPh$_3$]Cl; * denotes the isotropic peak.

thiocarbonyl carbon isotropic chemical shifts for the Imt ligand are also given in Table 4. The phosphorus nucleus in [ImtAgPPh$_3$]Cl is deshielded by 51 ppm relative to the free ligand, whereas in the other two complexes the phosphorus nucleus is only slightly shielded by about 3 ppm. In the phosphine complex the phosphorus is directly attached to the Ag and as such we expect the largest change. The reduction in electron density around the phosphorus nucleus leading to large de shielding can be rationalized due to the donation of phosphorus lone pair to the Ag atom. In [ImtAgSePPh$_3$]Cl complex the σ_{11} and σ_{22} components are shielded relative to the PPh$_3$Se ligand. Therefore, it can be postulated that the meta-ligand vector is oriented perpendicular to these two components, as the shielding effect is maximal in the direction perpendicular to this vector [26]. The ^{77}Se spectrum of [ImtAgSePPh$_3$]Cl showed two isotropic peaks along with J coupling to phosphorus. The ligand PPh$_3$Se also showed [27] two isotropic peaks indicating two molecules in a unit cell. However, only one phosphorus environment was observed in the free ligand as well as in the complex. The selenium resonance is deshielded by about 9 ppm on complexation. The carbon resonances of the thiocarbonyl carbons in the complexes are shielded by about 12 to 17 ppm relative to the free ligand [28].

3.6. Bioactivity studies

The results of the bioactivity studies are given in Table 5. No major difference in antimicrobial activity was observed between free ligand Imt and its complex with AgNO$_3$. The phosphine ligands

also show very little activity. However, after complexing with trans phosphine to the Ag(Imt)Cl complex, the antimicrobial activity has improved. It should be noted that the other two complexes namely [ImtAgSPPh_3]Cl and [ImtAgSePPh_3]Cl, do not show any antimicrobial activity. These results are important because thione ligand can be in equilibrium with its thiol form, so these data can be related to thiol containing complexes [18] as well.

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