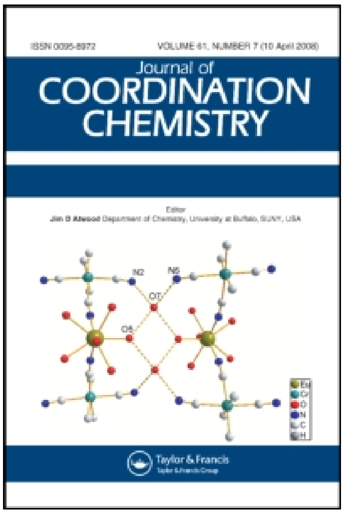

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Synthesis and Spectroscopic Characterization of Silver(I) Complexes of Selenones

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF SILVER(I) COMPLEXES OF SELENONES

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Silver(I) complexes of selenones, [LAgNO$_3$] and [AgL$_2$]NO$_3$ (where L is imidazolidine-2-selenone or diazinane-2-selenone and their derivatives) have been prepared and characterized by elemental analysis, IR and NMR (^{1}H, ^{13}C and ^{107}Ag) spectroscopy. An upfield shift in the C=Se resonance of selenones in ^{13}C NMR and a downfield shift in N–H resonance in ^{1}H NMR are consistent with selenium coordination to silver(I). In ^{107}Ag NMR, the AgNO$_3$ signal is deshielded by 450–650 ppm on coordination to selenones. Greater upfield shifts in ^{13}C NMR were observed for [LAgNO$_3$] compared to [AgL$_2$]NO$_3$ complexes, whereas the opposite trend was observed for ^{1}H and ^{107}Ag NMR chemical shifts.

Keywords: Silver(I) complexes; Selenones; NMR; Spectroscopy

INTRODUCTION

Recent research has 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 [1,2]. Therefore, a systematic investigation of silver complexation with selenium-containing ligands is important from a biological point in view. In spite of this importance, there is no known report describing the complexation of silver(I) with selenone ligands. Recently, we reported the synthesis and spectroscopic characterization of silver(I) complexes of selenourea [3]. The present report describes the synthesis of silver(I) complexes of stoichiometries, [LAgNO$_3$] and [AgL$_2$]NO$_3$ for a series of selenones and their characterization by ^{1}H, ^{13}C and ^{107}Ag NMR spectroscopy. It appeared to us that the combined use of ^{13}C and ^{107}Ag NMR would provide a powerful means for characterization of silver complexes in solution. The study also provides a useful database for ^{13}C and ^{107}Ag NMR spectra for silver(I) complexes of selenones.

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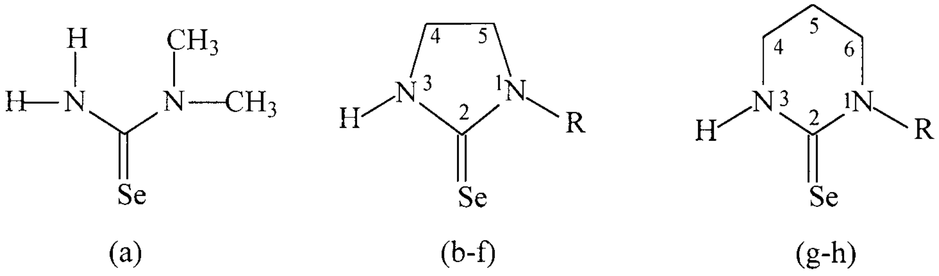

SCHEME 1 (a) *N*,*N*-dimethylselenourea (DmSeu); (b) R=H, Imidazolidine-2-selenone (ImSe); (c) R=CH_3, *N*-methylimidazolidine-2-selenone (MeImSe); (d) R=C_2H_5, *N*-ethylimidazolidine-2-selenone (EtImSe); (e) R=*i*-C_3H_7, *N*-(*i*-propyl)imidazolidine-2-selenone (*i*-PrImSe); (f) R=C_6H_5, *N*-phenylimidazolidine-2-selenone (PhImSe); (g) R=H, 1,3-Diazinane-2-selenone (DiazSe); (h) R=CH_3, *N*-methyl-1,3-Diazinane-2-selenone (MeDiazSe).

The structures of the selenones used in this study are described in Scheme 1.

EXPERIMENTAL

Chemicals

N,*N*-dimethylselenourea, acetonitrile, acetone, and DMSO-d_6 were obtained from Fluka. The selenone ligands were synthesized according to procedures described in the literature [4,5].

Preparation of Complexes

All complexes were prepared by mixing solutions of selenones and $AgNO_3$ in acetonitrile in molar ratios of 1 : 1 and 2 : 1, and stirring for 15 min. The resulting white precipitates were filtered and washed with acetonitrile or acetone. For the complexes $[Ag(EtImSe)_2]NO_3$, [*i*–PrImSeAgNO_3], [Ag(*i*–PrImSe)$_2$]NO_3 and $[Ag(DiazSe)_2]NO_3$ mixing resulted in colourless solutions, which after refrigeration yielded white crystalline products. After preparation, the complexes were stored in a refrigerator. The experimental yield of the products was around 60–70%. Elemental analyses and melting points of the complexes are given in Table I.

Spectroscopic Measurements

Solid state IR spectra were recorded on a Perkin Elmer FTIR 180 spectrophotometer using KBr pellets over the range 4000–400 cm^{-1}. All NMR measurements were carried out on a Jeol JNM-LA 500 NMR spectrophotometer at 297 K using 0.10 M solutions of the complexes (0.25 M for $[DmSeuAgNO_3]$) in DMSO-d_6. ^1H NMR spectra were obtained at 500.00 MHz. ^{13}C NMR spectra were obtained at 125.65 MHz with ^1H broadband decoupling and are referenced to TMS. Conditions were 32 k data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle.

^{107}Ag NMR was obtained at 20.13 MHz using a 10 mm low frequency probe with 9.1 M aqueous $AgNO_3$ as external reference. Conditions were 32 k data points, 1.02 s acquisition time, 6.0 s delay time, 45° pulse angle, and approximately 2000 scans.

TABLE I Elemental analyses of the silver(I) complexes of selenones

Complex	*(Found Calcd)%*			*m.p.* (°C)
	C	*H*	*N*	
[DmSeuAgNO_3]	11.13 (11.23)	2.47 (2.51)	12.79 (13.10)	79–80 (decomp)
[Ag(DmSeu)$_2$]NO_3	15.23 (15.27)	3.41 (3.42)	14.53 (14.84)	165–166
[ImSeAgNO_3]	11.43 (11.30)	1.85 (1.90)	13.06 (13.18)	128–129 (decomp)
[Ag(ImSe)$_2$]NO_3	15.56 (15.40)	2.58 (2.58)	14.87 (14.97)	138–140
[MeImSeAgNO_3]	14.62 (14.43)	2.44 (2.42)	12.45 (12.62)	107 (decomp)
[Ag(MeImSe)$_2$$NO_3$	19.52 (19.37)	3.48 (3.25)	14.10 (14.12)	164–165
[EtImSeAgNO_3]	16.74 (17.31)	2.78 (2.90)	11.46 (12.11)	106 (decomp)
[Ag(EtImSe)$_2$]NO_3	22.87 (22.92)	4.01 (3.85)	13.06 (13.37)	107–109
[*i*-PrImSeAgNO_3]	19.18 (19.96)	3.20 (3.35)	11.01 (11.64)	86–88
[Ag(*i*-PrImSe)$_2$]NO_3	25.61 (26.10)	4.11 (4.38)	12.32 (12.69)	83–86
[PhImSeAgNO_3]	27.27 (27.36)	2.60 (2.55)	10.54 (10.64)	116 (decomp)
[Ag(PhImSe)$_2$]NO_3	34.70 (34.86)	3.42 (3.25)	11.27 (11.30)	186–188
[DiazSeAgNO_3]	13.77 (14.43)	2.40 (2.42)	11.71 (12.62)	133–134
[Ag(DiazSe)$_2$$NO_3$	20.52 (19.37)	3.53 (3.25)	14.19 (14.12)	193–195
[MeDiazSeAgNO_3]	17.19 (17.31)	2.88 (2.90)	11.86 (12.11)	100–102

RESULTS AND DISCUSSION

Table II lists significant IR bands of free selenones and their silver(I) complexes. In IR spectra, the ν(C=Se) vibration, which occurs around 600 cm^{-1} for the free ligands [6] shifts towards lower frequency upon complexation, similar to findings for analogous thione complexes [7–9]. Another important vibrational band observed in the IR spectra of the selenones is ν(NH), which appears around 3200 cm^{-1}. Upon coordination to $AgNO_3$ this band shifts to higher wave numbers with some exceptions. A sharp band around 825 cm^{-1} for NO_3^- bending was observed for all complexes, indicating their ionic nature [10,11]. The presence of a band around 3200 cm^{-1} in free ligands as well as in the complexes indicates the existence of the selenone form of the ligands in the solid state.

Molar conductivity measurements in DMSO show that all complexes are 1 : 1 electrolytes, suggesting that the NO_3^- ion is either weakly coordinated or uncoordinated to silver(I). The molar conductance of free $AgNO_3$ ion DMSO was found to be 38.0 mho $cm^2\,mol^{-1}$. The molar conductivity of the complexes was found around 30–40 mho $cm^2\,mol^{-1}$ except for [Ag(ImSe)$_2$]NO_3, 16.8 mho $cm^2\,mol^{-1}$

^{1}H and ^{13}C NMR chemical shifts of 0.10 M solutions of the complexes in DMSO-d_6 are summarized in Table III. In ^{1}H NMR spectra of the complexes, N–H signals of the selenones became less intense upon coordination and shift downfield by 0.7–1.0 ppm from their positions in the free ligands. Deshielding of the N–H proton is related to an increase of π electron density in the C–N bond upon complexation [12]. The appearance of the N–H signal shows that the ligands coordinate to silver(I) *via* the selenone group.

In all complexes, the C-2 resonance appears upfield by 6–12 ppm compared to the free ligands, in accordance with data observed for metal complexes of analogous thiones [11,13,14]. The upfield shift is attributed to a lowering of the >C=Se bond order upon coordination and a shift of the N→C electron density producing a partial double bond character in the C–N bond [12,15]. The upfield shift decreases as the number of ligands attached to silver(I) increases from one in [L$AgNO_3$] to two in

TABLE II IR frequencies, $\nu(\mathrm{cm}^{-1})$ of the selenones and their complexes

Species	$\nu(C{=}Se)$	$\nu(NH)$	$\delta(NO_3^-)$
DmSeu	594	3260	
[DmSeuAgNO$_3$]	548	3304	824
[Ag(DmSeu)$_2$]NO$_3$	562	3270	828
ImSe	558	3254	
[ImSeAgNO$_3$]	566	3222	834
[Ag(ImSe)$_2$]NO$_3$	572	3212	826
MeImSe	580	3184	
[MeImSeAgNO$_3$]	572	3210	834
[Ag(MeImSe)$_2$]NO$_3$	562	3222	822
EtImSe	588	3198	
[EtImSeAgNO$_3$]	581	3234	834
[Ag(EtImSe)$_2$]NO$_3$	580	3216	824
i-PrImSe	600	3200	
[*i*-PrImSeAgNO$_3$]	598	3262	824
[Ag(*i*-PrImSe)$_2$]NO$_3$	600	3204	832
PhImSe	596	3190	
[PhImSeAgNO$_3$]	542	3176	822
[Ag(PhImSe)$_2$]NO$_3$	548	3176	822
DiazSe	602	3198	
[DiazSeAgNO$_3$]	588	3214	828
[Ag(DiazSe)$_2$]NO$_3$	586	3260	828
MeDiazSe	596	3214	
[MeDiazSeAgNO$_3$]	584	3244	826

TABLE III ^{1}H and ^{13}C chemical shifts of selenones and their silver(I) complexes

Species	*N–H*	*C-2*	*C-4*	*C-5*	*C-6*	*N–C1*	*N–C2*
DmSeu	7.53	177.69				45.32*	
[DmSeuAgNO$_3$]	8.57	165.63				45.83	
[Ag(DmSeu)$_2$]NO$_3$	8.26	169.91				45.68	
Imse	8.48	177.09	44.94	44.94			
[ImSeAgNO$_3$]	9.56	166.12	45.60	45.60			
[Ag(ImSe)$_2$]NO$_3$	9.29	170.48	45.31	45.31			
MeImSe	8.47	178.67	42.07	50.35		35.06	
[MeImSeAgNO$_3$]	9.29	167.29	43.05	51.59		35.58	
[Ag(MeImSe)$_2$]NO$_3$	9.09	171.45	42.72	51.25		35.43	
EtImSe	8.44	177.72	42.17	47.21		42.14	11.93
[EtImSeAgNO$_3$]	9.21	167.79	42.96	48.43		43.14	12.28
[Ag(EtImSe)$_2$]NO$_3$	9.08	171.04	42.70	48.14		42.88	12.21
i-PrImSe	8.43	177.18	42.28	47.72		42.26	19.10
[*i*-PrImSeAgNO$_3$]	9.24	166.22	42.98	49.66		43.67	19.50
[Ag(*i*-PrImSe)$_2$]NO$_3$	9.00	170.39	42.61	48.98		43.17	19.30
PhImse	9.02	177.22	42.61	51.74		140.81	128.20[a], 125.61[b], 124.67[c]
[PhImSeAgNO$_3$]	9.89	168.66	43.76	53.41		138.79	129.36[a] 128.20[b], 125.99[c]
[Ag(PhImSe)$_2$]NO$_3$	9.83	177.72	43.35	53.20		139.19	129.33[a], 127.92[b], 126.07[c]
DiazSe	8.23	169.14	40.10	18.76	40.10		
[DiazSeAgNO$_3$]	9.31	157.22	40.61	17.73	40.61		
[Ag(DiazSe)$_2$]NO$_3$	8.87	163.24	40.22	18.15	40.22		
MeDiazSe	8.38	172.65	39.95	20.39	44.02	47.39	
[MeDiazSeAgNO$_3$]	9.06	160.61	40.46	19.36	44.68	49.10	

*Another resonance at 38.07 ppm; [a]N–C2/6; [b]N–C4; [c]N–C3/5.

$[AgL_2]NO_3$. This is because of the increased number of electronegative groups attached to silver(I). A small shift of 1–2 ppm is seen for other carbon atoms, which shows that nitrogen atoms are not involved in coordination. In complexes of ImSe and its derivatives, a deshielding effect was observed at C-4/5. While in DiazSe and MeDiazSe complexes a deshielding effect was observed at C-4 and C-6, C-5 exhibited a shielding effect. The deshielding at C-4/6 is due to an increase in the π character of the C–N bond. N–CH_3 carbons in free DmSeu give two signals showing that they are non-equivalent. However, after complexation only one signal is observed. The difference in shielding at C-2 may be related to the strength of the metal-selenium bond, which arises from back donation of silver(I) to selenium [12]. The smallest complexation shifts were observed for PhImSe complexes, while the most significant shifts were observed for DmSeu complexes. This shows that DmSeu complexes are the most stable, while PhImSe complexes are least stable.

A comparison of shift differences in the C-2 resonance of selenones and thiones is given in Table IV. It is seen that shifts are greater for the selenone complexes than for the thione ones, showing that selenones form more stable complexes with silver(I). This trend is expected, since selenium, being softer compared to sulfur, would prefer to bind more strongly to a softer metal.

In ^{107}Ag NMR the signal for $AgNO_3$ is deshielded by 166 ppm when recorded in DMSO, compared to aqueous solution, showing that the ^{107}Ag chemical shift is not only sensitive to the nature of ligands but is also affected by changing solvent. Complexation with selenones shifts the signal further downfield by 450–650 ppm. This very large reduction in shielding seems to be due to silver(I) binding to the selenium of the selenones [16]. In the case of bonding through nitrogen, a smaller shift of around 100 ppm would have been observed in ^{107}Ag NMR [16]. This provides clear evidence that selenones bind to silver(I) through selenium only. ^{107}Ag chemical shifts of all complexes are listed in Table V.

The greater downfield shifts in ^{107}Ag NMR for bis complexes as compared to mono complexes occur because of the increased number of electronegative groups attached to silver(I). As observed in the ^{13}C NMR data, the shift is largest for DmSeu complexes and smallest for PhImSe complexes. Thus ^{107}Ag NMR also suggests that DmSeu forms the most stable complex with silver(I), while PhImSe forms the least stable among the selenones. For $[Ag(ImSe)_2]NO_3$, the silver resonance appears upfield compared to its mono complex, suggesting that the compound may be polymeric, since a

TABLE IV Comparison of differences in the ^{13}C and ^{107}Ag NMR chemical shifts for silver(I) complexes of thiones and selenones in DMSO-d_6

Thione complexes	$\Delta\delta$ (^{13}C)[a]	$\Delta\delta$ (^{107}Ag)[b]	*Selenone complexes*	$\Delta\delta$ (^{13}C)[c]	$\Delta\delta$ (^{107}Ag)
$[ImtAgNO_3]$	6.48	405.0	$[ImSeAgNO_3]$	10.97	549.9
$[Ag(Imt)_2]NO_3$	5.63	442.3	$[Ag(ImSe)_2]NO_3$	6.61	473.1
$MeImtAgNO_3$	5.87	327.7	$[MeImSeAgNO_3]$	11.38	526.3
$[Ag(MeImt)_2]NO_3$	4.63	479.4	$[Ag(MeImSe)_2]NO_3$	7.22	559.7
$[EtImtAgNO_3]$	5.22	314.2	$[EtImSeAgNO_3]$	9.93	500.1
$[Ag(EtImt)_2]NO_3$	4.79	479.2	$[Ag(EtImSe)_2]NO_3$	6.69	510.9
[*i*-PrImtAgNO$_3$]	5.18	323.6	[*i*-PrImSeAgNO$_3$]	10.96	495.9
[Ag(*i*-PrImt)$_2$]NO$_3$	4.97	484.3	[Ag(*i*-PrImSe)$_2$]NO$_3$	6.79	511.7
$[EtDiazAgNO_3]$	7.98	446.0	$[MeDiazSeAgNO_3]$	12.04	446.0

[a]C-2 resonance of thiones; [b]W.r.t. free $AgNO_3$ in DMSO; [c]C-2 resonance of selenones.

TABLE V ^{107}Ag chemical shifts of various silver(I)–selenone complexes in DMSO-d_6

Selenone (L)	*δ (^{107} Ag) for [LAgNO$_3$]*	*δ (^{107}Ag) for [AgL$_2$]NO$_3$*
DmSeu	748.6	839.8
ImSe	715.9	639.1
MeImSe	692.3	725.7
EtImSe	666.1	676.9
i-PrImSe	661.9	677.7
PhImse	615.6	625.4
MeDiaz	612.0	

δ(^{107}Ag) for AgNO$_3$ in DMSO = 166.0 ppm.

similar trend was observed for [Ag(Tu)$_x$NO$_3$] ($x = 1$–4) and silver-thione complexes, which are also polymeric [14,17–19]. A comparison of silver chemical shifts for the silver(I) complexes of the thiones [14] and selenones (Table III) shows that downfield shifts for the selenone complexes are larger than those of the thione complexes, possibly because selenium is more polarizable than sulfur.

In this study, we have shown that selenones react with silver nitrate to form complexes of the type [LAgNO$_3$] and [AgL$_2$]NO$_3$ in which the ligands exist in the selenone form both in solution as well as in the solid state. Chemical shifts for different complexes presented here would be useful, especially if ^{107}Ag NMR is used, to study silver(I) complexes with selenium-containing ligands in biological systems.

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