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The Vibrational Spectra and Molecular Structure of Some Silver Pseudohalide Complex Anions

O. H. ELLESTAD,[a] P. KLÆBOE,[a] E. E. TUCKER[a] and J. SONGSTAD[b]

[a]*Department of Chemistry, University of Oslo, Oslo 3, Norway, and* [b]*Chemical Institute, University of Bergen, N-5000 Bergen, Norway*

The following complex silver compounds $(CH_3)_4NAg(CN)$, $(C_6H_5)_4AsAg(CN)_2$, $(CH_3)_4NAg(NCO)_2$, $(C_6H_5)_4AsAg(NCO)_2$, $(CH_3)_4NAg(SCN)_2$, and $(CH_3)_4NAg(SeCN)_2$ were studied by vibrational spectroscopy. IR spectra of the solids (CsI pellets, polyethylene pellets, Nujol mulls) were recorded in the region 4000–45 cm^{-1} and the saturated solutions in acetonitrile investigated between 4000 and 350 cm^{-1}. Raman spectra of the compounds were recorded in the solid state and as saturated solutions in acetonitrile, and semiquantitative polarization measurements of the strong Raman bands were carried out.

The spectra indicate that the anions exist as dicyanoargentate $Ag(CN)_2^-$, diisocyanatoargentate $Ag(NCO)_2^-$, dithiocyanatoargentate $Ag(SCN)_2^-$ and diselenocyanatoargentate $Ag(SeCN)_2^-$, each having the silver atom in a symmetry centre. The spectra have been interpreted in terms of $D_{\infty h}$ and C_{2h} molecular structures. The fundamental frequencies of the complex silver anions have been tentatively assigned.

It is well known that the Ag^+ ion can form complex cations like $Ag(NH_3)_2^+$ [1,2] and anions $Ag(CN)_2^-$ [3,4] which are linear in the solid and in solution. However, X-ray crystallographic studies of $NH_4Ag(SCN)_2$ [5] revealed that the crystals consist of AgSCN molecules and ammonium and thiocyanate ions and that $KAg(SeCN)_2$ [6] correspondingly contained AgSeCN molecules and potassium and selenocyanate ions. Accordingly, in these compounds there are no symmetric anions like $Ag(SCN)_2^-$ or $Ag(SeCN)_2^-$, but one ionic and one covalently bonded pseudohalide group are found. Moreover, in complex silver halides $(CH_3)_4NAgX_2$ (X = Cl or Br) far-IR data indicate no AgX_2^- ions in the crystal,[7] since infinite chains of $[AgX_4]$ units are proposed. However, AgX_2^- ions seem to be present in dimethyl sulphoxide solutions. To determine if the latter ions are linear or bent additional information is required, *e.g.*, Raman data. It has been reported from dipole measurements [8] that in AgI_2^- the I–Ag–I angle is 111° in solution, close to the tetrahedral angle. Generally, it has been concluded that ligands which are strong Lewis bases should favour linear dicoordinated complexes with the silver ion.[9]

We have for some time been interested in inorganic complexes including pseudohalides [10,11] and have recently discussed the diisocyanatoargentate ion.[12] In the present paper we report a study of six silver pseudohalide complex anions by infrared and Raman spectroscopy. It was convenient to use large, bulky onium ions as counterions in the salts since these cations have only weak polarizing effect on the anions. Moreover, the diisocyanatoargentate ion decomposes rapidly in the presence of small metal cations.[12] With tetramethyl ammonium and tetraphenyl arsonium ions some of these salts were readily soluble in aprotic solvents like acetonitrile which facilitated recording of the solution spectra. It was found that the two onium cations had practically identical IR and Raman spectra, respectively, throughout the series. In order to separate the cation bands from those of the silver anions, a few single onium salts were prepared and their spectra are reported separately.[13]

From the empirical characteristic frequency correlations proposed for the present ligands it should be possible to decide whether they are cyanates or isocyanates and thio(seleno) cyanates or isothio(isoseleno) cyanates. Particularly, we want to establish if the silver salts exist as: (1) complex anions Ag-$Ligand_2^-$, or (2) separate neutral entities as Cat Ligand + Ag Ligand, or (3) bridged oligomeric or polymeric structures ($Ligand_2$ Ag $Ligand_2$ Ag $Ligand_2$ Ag$\cdots)^{n-}$ (Cat = cation).

By comparing the spectra recorded of the solids with those of the solutions, structural changes, *e.g.* between (1), (2) or (3), should be detected. If the compounds are found to exist as Ag $Ligand_2^-$ anions it is of interest to determine if they have a symmetry centre and possibly if they are linear or bent. An assignment of the fundamental vibrational frequencies of the present species will be attempted. Many spectral studies of metal pseudohalide complexes have been concerned with the IR spectra, but very few Raman studies have so far been reported.

EXPERIMENTAL

Chemicals. Tetramethylammonium dicyanoargentate was made from purified and dried tetramethylammonium chloride and freshly prepared silver cyanide in acetonitrile. Recrystallized twice from acetonitrile, the compound had m.p. 194 – 195°C.

Tetraphenylarsonium dicyanoargentate was made as reported previously.[10] M.p. 169 – 170°C.

The syntheses of tetramethylammonium isocyanatoargentate, m.p. 123 – 124°C, and tetraphenylarsonium diisocyanatoargentate, m.p. 155°C, have recently been reported.[12]

Tetramethylammonium dithiocyanatoargentate was made in near quantitative yield from tetramethylammonium thiocyanate and an equivalent amount of silver thiocyanate in acetonitrile. The compound was recrystallized from acetonitrile, m.p. 134 – 136°C.

Tetramethylammonium diselenocyanatoargentate was made likewise. M.p. 137 – 138°C (acetonitrile). Due to the rather limited solubility of the last two products in acetonitrile, these compounds were easily separated from traces of unreacted tetramethylammonium thiocyanate and selenocyanate. All the melting points are corrected.

Instrumental. The IR spectra were recorded using a Perkin-Elmer model 225 spectrometer in the region 4000 – 200 cm^{-1} and a Hitachi-Perkin Elmer FIS-3 spectrometer for the far-IR region (400 – 45 cm^{-1}). The solid samples were investigated as KI, CsI, and polyethylene (Rigidex) pellets and as Nujol mulls. Saturated solutions of the complex salts were prepared in anhydrous acetonitrile and the solutions were filled into sealed

cells of thickness 0.1 and 0.025 mm having KBr-windows or 0.2 mm cells with windows of polyethylene.

A Cary model 81 Raman spectrometer equipped with a Spectra Physics model 125A helium-neon laser was employed for the Raman recordings. The solid samples were filled into tubes with flat ends placed against the hemispherical lens. Capillary tubes of approximately 1 mm inner diameter were filled with the saturated acetonitrile solutions. The samples of $Me_4NAg(NCS)_2$ and $Me_4NAg(NCSe)_2$ were not sufficiently soluble to give Raman spectra in solution. On the other hand the argentocyanides and argentoisocyanates gave fairly intense Raman spectra in solution and semiquantitative polarization measurements of the strong bands were carried out.

RESULTS AND DISCUSSION

Argento cyanide ion. The observed vibrational frequencies for $(CH_3)_4NAg(CN)_2$ and $(C_6H_5)_4AsAg(CN)_2$ in the solid state and in acetonitrile solution are listed in Tables 1 and 2, respectively. It is shown by X-ray crystallography that in $KAg(CN)_2$ the $Ag(CN)_2^-$ ion is linear.[3] Extensive IR and Raman spectral studies [4,14,15] on alkali salts of $Ag(CN)_2^-$ and $Au(CN)_2^-$ including isotopic species and oriented single crystals indicate linear arrangements in the crystal and in aqueous solution. More recently far-IR data [16] and new Raman measurements [17] for $KAg(CN)_2$ were reported, which also indicated linear arrangements. The vibrational studies [14] as well as broad line NMR work [18] strongly suggest that in $KAg(CN)_2$ the carbon atom is bonded to silver. Generally, all metal cyano complexes are considered to be real cyanides.

Our present results for $(CH_3)_4NAg(CN)_2$ and $(C_6H_5)_4AsAg(CN)_2$ reveal mutual exclusion of IR and Raman frequencies for the $Ag(CN)_2^-$ ions. Accordingly, we can assume centres of symmetry in the crystals and the existence of $Ag(CN)_2^-$ ions in the present two compounds. Any "separate entities" Cat Ligand + Ag Ligand or bridged polymeric structures can therefore be ruled out. Furthermore, the number of observed bending fundamentals are consistent with a linear arrangement (NC – Ag – CN). Since the M – CN linkage always appears to be linear, the existence of a symmetry centre independently imposes a linear arrangement on the $Ag(CN)_2^-$ ion. With point group $D_{\infty h}$, the seven fundamentals will divide themselves between the following species: $2\Sigma_g^+$, $2\Sigma_u^+$, 1 Π_g and 2 Π_u, of which the g and u modes are Raman and IR active, respectively. The Σ_g^+ vibrations will be polarized and those of species Π_g will be depolarized. In the absence of IR vapour spectra no direct experimental evidence can distingusih between the stretching modes Σ_u^+ and the doubly degenerate bending mode Π_u, insofar as no crystal splitting was observed in the IR or Raman spectra.

The assigned fundamentals of the $Ag(CN)_2^-$ anions of $(CH_3)_4NAg(CN)_2$ and $(C_6H_5)_4AsAg(CN)_2$ are listed in Table 3. Because of the relatively low solubility of these compounds in acetonitrile, weak bands were not detected in solution, and therefore only the solid state frequencies are given in Table 3. However, the close similarity between the solid and solution frequencies indicates no significant change in geometry or in bonding of the $Ag(CN)_2^-$ ions between the two states.

The assigned fundamental frequencies listed in Table 3 agree quite well with those reported for $KAg(CN)_2$,[14–17] and only slight frequency differences between the two present compounds were observed. The Raman active, sym-

Table 1. Infrared and Raman spectral data of $(CH_3)_4NAg(CN)_2$ (2300 – 45 cm^{-1}).

Infrared		Raman	
Solid Pellet [a]	Solution CH_3CN	Solid Powder	Solution CH_3CN
		2138 s *	2142 s, P *
2122 s *[b]	2128 m *		
1487 vs	1486 m		
1453 w		1461 m	
		1450 w,sh	
1414 w		1415 vw,bd	1418 vw,bd
1406 m			
1398 m			
1293 w,bd		1293 vw,bd	1295 vw
		1273 vw,bd	
		1177 vw,bd	1179 vw,bd
950 vs	947 m	950 m	954 m, D
944 vs			
918 w			
917 w			
		754 m	755 s
		735 vw,sh	735 vw
		493 vw	495 vw
467 w			
457 w		458 m	460 w
389 m *			
		375 vw,bd	
		350 w,bd *	
311 vw,sh			
292 m *			
274 m			
253 vw,sh		253 w	
		238 m *	242 s, D *
145 m,bd			
116 m,bd *			
80 m,bd			
		75 w,sh	

Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad; P, polarized and D, depolarized.

[a] Cesium iodide (2500 – 250 cm^{-1}), polyethylene (400 – 45 cm^{-1}).

[b] Bands marked with an asterisk are attributed to the $Ag(CN)_2^-$ ion.

metric C≡N stretching frequencies ν_1 were higher than the IR active, asymmetric frequencies ν_3. As reported for $KAg(CN)_2$ [14,17] very weak Raman bands around 360 cm^{-1} with no polarization ratios obtainable were attributed to the symmetric Ag – C stretching modes ν_2. Medium intense IR bands at 389 and 385 cm^{-1} were assigned to the corresponding asymmetric Ag – C stretching vibrations ν_4 in the two compounds.

The Raman active bending modes ν_5 were observed at 238 and 242 cm^{-1} in the solid state spectra, appearing depolarized in solution. We have assigned the IR bands at 292 and 297 cm^{-1} to ν_6 in excellent agreement with the value

Table 2. Infrared and Raman spectral data of $(C_6H_5)_4AsAg(CN)_2$ (2500 – 45 cm^{-1}).

Infrared		Raman	
Solid Pellet [a]	Solution CH_3CN	Solid Powder	Solution CH_3CN
		2136 s *	2143 s, P *
2128 m,sh 2123 m *[b]	2129 m		
2112 w,sh			
		1580 s	1584 s, D
1479 s	1483 m	1480 w	
1472 w,sh			
		1442 w	
1437 s			
1393 vw			
1383 vw		1384 vw	
		1344 vw	
1334 w	1337 vw		
1312 w 1307 w	1312 vw	1314 vw	
1278 vw		1280 vw	
1182 w	1185 w	1181 s	1191 w,bd
1164 w		1166 s	1168 w,bd
1100 vw,sh			
		1086 s	1087 m
1080 s	1080 s		
1067 w			
		1026 s	1027 s, D
1022 m			
999 s	997 s	1003 vs	1004 vs, P
		933 m	
918 w			
911 vw			
		858 w,bd	
847 vw			
		755 w	753 vw
740 vs			
688 s	689 s		
682 s		682 m,sh	
		674 vs	674 s, P
668 w,sh			
614 w		618 s	617 m
		495 vw	495 vw
474 s	476 s		
463 m,sh		465 m	
457 s	463 s		
		442 vw	
		397 vw	
385 m *			
		367 w *	
353 s		356 w,sh	
347 m		347 m	
297 w *		300 w,sh	
		274 m	268 m
		260	

Table 2. Continued.

245 vw	242 s *	240 s, D *
229 vw		
183 w	186 s	185 m
110 m *		
	105 w	
96 m,sh	95 w,sh	
	75 w,sh	
46 vw		

For abbreviations, see footnote to Table 1. [a] Potassium iodide (2500–300 cm^{-1}), polyethylene (400–45 cm^{-1}). [b] Bands marked with an asterisk are attributed to the $Ag(CN)_2^-$ ion.

291 cm given for $KAg(CN)_2$.[16] Finally, the lowest bending modes ν_7 are attributed to the medium intense IR bands at 116 and 110 cm^{-1} for the two compounds since no other suitable absorption bands were detected in this region. Most of the IR and Raman bands not attributed to the $Ag(CN)_2^-$ anions agree well with the frequencies observed [13,19,20] for the cations $(CH_3)_4N^+$ and $(C_6H_5)_4As^+$.

Argento isocyanate ion. The observed vibrational frequencies for $(CH_3)_4NAg(NCO)_2$ and $(C_6H_5)_4AsAg(NCO)_2$ in the solid state and in acetonitrile solution are listed in Tables 4 and 5, respectively. It is apparent from the compiled frequencies that the strong or medium intense IR or Raman bands of the solids were observed in solution, except when covered by solvent bands. Thus, it seems safe to conclude that no significant structural change of the cations or anions occurred upon solution. While the large majority of the bands in Tables 4 and 5 can be attributed to the cations [13] an assignment of the anion bands has been attempted. These tentatively assigned fundamentals for the anions $Ag(NCO)_2^-$ are listed in Table 6.

Practically all the investigated NCO coordination complexes are N-bonded,[21] *i.e.* they are *isocyanates*, although some O-bonded *cyanates* including Re^{IV}, Mo^{III},[22] Ti^{IV}, Zr^{IV}, and Hf^{IV} [23] have been suggested. The "free NCO^- ion" in the K^+ salt has the following fundamental frequencies:[24] 2165 (CN

Table 3. Vibrational fundamental frequencies [a] for the $Ag(CN)_2^-$ anions.

$(CH_3)_4NAg(CN)_2$	$(C_6H_5)_4AsAg(CN)_2$	Interpretation
2138	2136	Σ_g^+ ν_1 CN stretch
350	367	ν_2 AgC stretch
2122	2123	Σ_u^+ ν_3 CN stretch
389	385	ν_4 AgC stretch
238	242	Π_g ν_5 AgCN def
292	297	Π_u ν_6 AgCN def
116	110	ν_7 CAgC def

[a] The listed values are solid state frequencies.

Table 4. Infrared and Raman spectral data of $(CH_3)_4NAg(NCO)_2$ (2500 – 200 cm^{-1} i.r.).

Infrared		Raman	
Solid CsI Pellet	Solution CH_3CN	Solid Powder	Solution CH_3CN
		2218 vw *	2218 vw *
		2200 vw,sh	2205 vw,sh
2142 vs *[a]	2163 vs *		
2093 m	2110 m		
2082 w			
2037 vw			
1595 vw,bd			
1483 s	1488 s		
1478 m	1479 m,sh		
		1452 w	1454 m
1441 w			
		1420 vw,sh	1420 vw
1404 m			
1396 m			
		1336 w,sh	
		1320 s *	1328 s P *
1304 m	1324 m		
1287 s	1300 s		
1264 vw			
1256 vw *			
		1205 vw	1212 vw
1198 s	1207 s		
1180 m	1191 w		
1170 vw		1174 vw	1175 vw
951 s,sh	948 s	955 w	952 m
944 s			
917 w			
		760 m	753 s
			738 m,sh
658 w	663 w		
	637 s		
628 s *	627 s *	620 vw	
610 vw	616 m,sh	610 w *	616 vw,bd *
570 w	570 vw		
		490 vw,bd	490 vw,bd
		461 w	459 vw,bd
469 vw			
453 w	455 vw		
390 vw,bd *			
		375 w *	
263 vw			
		115 vw,sh	
		105 vw,sh	

For abbreviations, see footnote to Table 1.
[a] Bands marked with an asterisk are attributed to the $Ag(NCO)_2^-$ ion.

stretch), *ca.* 1254 (CO stretch) and 637 and 628 cm^{-1} (NCO bend) in which the 1254 cm^{-1} band is calculated from the two bands at 1301 and 1207 cm^{-1} in Fermi interaction. The extensive IR work on isocyanates and cyanates

Table 5. Infrared and Raman spectral data for $(C_6H_5)_4AsAg(NCO)_2$ (2500 – 45 cm^{-1}).

Infrared		Raman	
Solid Pellet [a]	Solution CH_3CN	Solid Powder	Solution CH_3CN
		2213 vw *	
2200 w	2198 w		
		2160 vw	
2145 vs *[b]	2143 s *		
2133 m,sh			
2122 w,sh			
2092 vw			
1578 vw		1583 s	1586 s, D
		1487 vw,bd	
1480 s			
1442 s,sh		1445 vw,bd	
1437 s			
		1388 vw,bd	
1337 w		1338 m *	1337 w, P *
1311 w			
1288 m *	1300 m *		
		1283 vw,bd	1293 vw
1197 m	1207 m		
		1191 w	1193 w
1186 w,sh	1188 vw		
1165 vw		1168 w	1169 w
		1086 m	1088 w
1081 s	1082 s		
		1026 s	1028 s, D
1022 w			
		1003 vs	1005 vs, D
997 s	998 s	990 vw,sh	
		928 vw,bd	
920 vw,bd			
845 vw			
750 m,sh		750 vw,bd	
740 s			
687 s	690 s	684 m,sh	
680 m,sh			
670 w,sh		675 s	676 s, D
627 m *	637 m *		
622 m,sh	627 m		
		616 m *	618 m, D*
		490 vw,bd	495 w,bd
474 s	477 m		
466 s	464 m	465 vw	
455 w		400 vw *	
390 vw,bd *			
365 w,sh			
352 s		355 w,bd	
344 s,sh			
		275 w	267 w,bd
		265 w,bd	

Table 5. Continued.

238 w	238 m	240 vs
182 w	187 m	
149 m *		
132 m *		
115 m,sh		
75 w	79 w	

For abbreviations, see footnote to Table 1.
[a] Cesium iodide (2500–250 cm^{-1}), polyethylene (400–45 cm^{-1}).
[b] Bands marked with an asterisk are attributed to the $Ag(NCO)_2^-$ ion.

indicates that for both classes of compounds the CN stretch is raised and the NCO bend changes slightly from the free ion frequencies.[21,23,25] However, the CO stretch is raised for isocyanates and lowered for cyanates compared to the free ion.[21,23,25,26] The fundamentals listed in Table 6 reveal N-bonding, since distinctly polarized Raman bands were observed around 1330 cm^{-1}, ascribed to the CO stretch of species Σ_g^+. Although less conclusive because of possible Fermi resonance between the overtone of the NCO bend and the IR active CO stretch (ν_5) the bands around 1288 cm^{-1} of species Σ_u^+ support this assumption.

The observed frequencies of Tables 4 and 5 attributed to the anions strongly indicate mutual exclusion between the IR and Raman bands as observed for the cyanides (Tables 1 and 2). Therefore, we can again rule out the existence of "separate entities" such as Cat Ligand + Ag Ligand or polymeric structures for these compounds and conclude that the anions exist as $(OCNAgNCO)^-$ with a symmetry centre. Generally organic isocyanates RNCO (R being H or C) are bent at the nitrogen [27] with reported angles between 125° and 142°. When R is silicon, linear arrangements have been reported from microwave work,[28] and in heavy metal atoms with *d*-electrons the hybridization can

Table 6. Tentative vibrational fundamental frequencies [a] for the $Ag(NCO)_2^-$ anions.

$(CH_3)_4NAg(NCO)_2$	$(C_6H_5)_4AsAg(NCO)_2$	Interpretation
2218	2213	Σ_g^+ ν_1 NC stretch
1320	1338	ν_2 CO stretch
375	400	ν_3 AgN stretch
2142	2145	Σ_u^+ ν_4 NC stretch
~1287	~1288	ν_5 CO stretch
390	390	ν_6 AgN stretch
610	616	Π_g ν_7 NCO bend
–	–	ν_8 AgNC bend
628	627	Π_u ν_9 NCO bend
–	149	ν_{10} AgNC bend
–	132	ν_{11} NAgN bend

[a] The listed values are solid state frequencies.

favour linear structures. In a recent X-ray crystallographic study [29] of $(CH_3)_4NAg(NCO)_2$ an approximately linear arrangement was observed with $\angle NAgN = 177.°$, $\angle OCN \approx 179°$ and $\angle CNAg \approx 171°$. From the electron density maps it was not possible to conclude with certainty if the structure was that of an isocyanate (as shown in this study) or a cyanate. Although we cannot with certainty decide between the point groups $D_{\infty h}$ (linear) or C_{2h} (bent) from the spectral data, the X-ray results [29] are consistent with a linear or nearly linear structure. It seems very probable that the CNAg linkage will also be linear in solution. In Table 6 the spectra of both compounds are accordingly interpreted in terms of linear arrangements ($D_{\infty h}$) with 11 fundamentals. With the bent arrangement (C_{2h}) each of the five bending modes should split into an in-plane and an out-of-plane component which did not appear likely from the solid state spectra.

Obviously, the four additional fundamentals in the $Ag(NCO)_2$ ions compared to the $Ag(CN)_2$ ions make the interpretations in Table 6 less certain than those in Table 3. Furthermore, the low frequency bending vibrations are more uncertain than the higher frequency bands, because of low intensities in the IR, broad Rayleigh wings in Raman and interfering solvent bands. The far IR spectrum of $(CH_3)_4NAg(NCO)_2$ was not recorded and the two lowest Π_u

Table 7. Infrared and Raman spectral data for $(CH_3)_4NAg(SCN)_2$ (2300 – 45 cm^{-1}).

Infrared Solid Pellet [a]	Raman Solid Powder	Infrared Solid Pellet [a]	Raman Solid Powder
	2112 vs *	733 vw,sh	
	2102 vs *	725 vvw	725 w *
2057 vs *[b]			600 vvw
1495 vw,sh			550 vvw
1483 s		484 w	489 vw,bd
1475 s		473 m *	
	1458 m		466 m,sh *
1440 w		458 vw,bd	458 s
1410 w	1415 w		478 m,sh
1402 w	1407 w,sh	363 vw	
1395 w		297 vvw	
1287 vw,bd	1289 vw	281 vvw *	
	1175 vw	198 vw	
973 w		170 vvw,sh	
951 m,sh	950 m	155 vvw	
947 s		130 vvw *	
918 vw,bd	918 vw,bd	115 w	
	900 vw,bd		105 vw *
	757 s	95 w *	95 w
750 m *			
744 w			

For abbreviations, see footnote to Table 1.
[a] Cesium iodide (2300 – 250 cm^{-1}), polyethylene (400 – 45 cm^{-1}).
[b] Bands marked with an asterisk are attributed to the $Ag(SCN)_2^-$ ion.

Table 8. Infrared and Raman spectral data for $(CH_3)_4NAg(SeCN)_2$ (2300 – 45 cm^{-1}).

Infrared		Raman
Solid Pellet [a]	Solution CH_3CN	Solid
2140 vw *[b]		
		2122 vs *
		2104 vs *
2085 vs *	2089 w*	
2057 s	2057 s	
1485 s		
		1455 s
		1443 m
1404 mw		
1398 w		
1393 vw		
1292 vw,bd		1292 w,bd
952 s	949 m	952 w
945 vs		
918 vw,bd		
815 vw,bd		
		789 vw
		776 vw
		756 m
		735 vw,sh
548 vw *		545 w,sh *
538 w *		539 w *
		493 w,bd
472 vw		
457 vw		458 w
432 vw		
421 vw		
411 vw *		
408 vw		
		395 m *
391 vw,sh		390 w,sh
381 vw		
		373 vw,bd
		123 w
115 m		
102 m,sh *		98 w *
		82 w,bd
61 w *		

For abbreviations, see footnote to Table 1.
[a] Cesium iodide (2300 – 250 cm^{-1}), polyethylene (400 – 45 cm^{-1}).
[b] Bands marked with an asterisk are attributed to the $Ag(SeCN)_2^-$ ion.

modes ν_{10} and ν_{11} remain unobserved. Moreover, none of the observed Raman bands agrees with the expected value for the lowest Π_g fundamental and ν_8 has therefore been left unassigned for both compounds.

Argento thio and selenocyanate ions. The observed IR and Raman frequencies for $(CH_3)_4NAg(SCN)_2$ and $(CH_3)_4NAg(SeCN)_2$ are listed in Tables 7 and 8,

Table 9. Tentative vibrational fundamental frequencies [a] for the $Ag(SCN)_2^-$ and $Ag(SeCN)_2^-$ anions.

$(CH_3)_4NAg(SCN)_2$	$(CH_3)_4NAg(SeCN)_2$	Interpretation		
2108 vs	2113 vs	A_g	ν_1	CN stretch
725 w	543 w		ν_2	CX stretch
466 m,sh	395 w		ν_3	XCN bend
–	–		ν_4	AgX stretch
105 vw	98 w		ν_5	AgXC bend
473 m	410 vw	A_u	ν_6	XCN bend
130 vw	102 m,sh		ν_7	AgXC bend
95 w	61 w		ν_8	XAgX bend
466 m,sh	395 m	B_g	ν_9	XCN bend
2057 vs	2071 s	B_u	ν_{10}	CN stretch
750 m	545 vw		ν_{11}	CX stretch
473 m	410 vw		ν_{12}	XCN bend
281 vw	–		ν_{13}	AgX stretch
130 vw	102 m,sh		ν_{14}	AgXC bend
95 w	61 w		ν_{15}	XAgX bend

[a] The listed values are solid state frequencies. [b] Interpreted in terms of C_{2h} symmetry with a bent AgSC angle, although $D_{\infty h}$ cannot be excluded from the spectra.

respectively. Because of very low solubilities in acetonitrile, no vibrational bands were detected in a saturated solution of the former and only a few IR bands in the latter. Our tentative fundamental frequencies for the anions are listed in Table 9.

Unlike the situation with cyanate coordination, thiocyanate and selenocyanate complexes can easily be N or X coordinated (X = S, Se) and many examples are known of both types as well as of linkage isomers.[22] In various reviews [21,30,31] the behaviour of the IR absorptions of thiocyanate and selenocyanate coordination complexes are treated. Several criteria have been proposed to distinguish between N and X-bonding including [22] the position and intensity of the CN stretching vibration, the frequencies for C – X stretching and NCX deformation as well as the Metal – N or Metal – X stretching modes. These values should be compared with those of the "free ions" (K^+ salts): CNS^-;[32] 2053, 746, 478 cm^{-1} and CNSe;[33] 2070, 558, 420 cm^{-1}.

Applied to the present silver complexes these criteria favour X-coordination based upon the following observations:

The average frequency of the IR and Raman active CN stretching vibrations (ν_1 and ν_4) are 2082 and 2098 cm^{-1} in the S and the Se compounds, respectively, which are higher than in the free ions and therefore support X-coordination.[34] The bands assigned to the CS or CSe stretching vibrations (ν_2 and ν_5 in Table 9) appear on the average lower than those of the free ions as expected for X-coordination.[35,36] The IR and Raman bands tentatively attributed to the SCN bending modes (ν_7 and ν_8) around 480 cm^{-1} might possibly suggest N-bonding [35,37] (X-bonding around 420 cm^{-1}). However, with considerable variation in these frequencies this criterion seems quite uncertain. Thus, the spectral data strongly support X-bonding for both compounds as

expected since the "soft" Ag should interact [38] with the "soft" S or Se atoms in preference to the "hard" nitrogen atom.

In spite of some possible IR-Raman coincidences (which might be accidental) the spectral data seem compatible with symmetry centres for both the anions. Accordingly, the possible "separate entities" Cat Ligand + Ag Ligand or bridged structures which are quite common among thiocyanates [39] can be excluded. Whether the $Ag(SCN)_2^-$ or $Ag(SeCN)_2^-$ anions are linear ($D_{\infty h}$) or bent (C_{2h}) cannot be inferred except from the number of bending modes (5 for $D_{\infty h}$ or 10 for C_{2h}). The relatively small number of low frequency IR and Raman bands might suggest a linear structure, although the frequently observed pairs of neighbouring bands might be due to in-plane and out-of-plane vibrations. Interference from the $(CH_3)_4N^+$ cations and the less complete spectra for these compounds make the data ambiguous. The tentative fundamentals in Table 9 are assigned in terms of C_{2h} symmetry. Although not prominent in these molecules, the appearance of factor group splitting cannot be excluded. Without polarization measurements the fundamentals are listed as accidentally degenerate although we have observed some weak splittings.

It is a significant result of the present study that in the presence of weakly polarizing bulky onium counterions stable $Ag(SCN)_2^-$ and $Ag(SeCN)_2^-$ ions are present. In salts of small cations like K^+ or NH_4^+, however, the silver coordination is reduced and AgS(Se)CN + K(NH$_4$)S(Se)CN entities are present in the solid.[5,16] The nature of the cation apparently has a pronounced effect upon the silver coordination.

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