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Silver-109 NMR Spectroscopy of Inorganic Solids

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In this study the ^{109}Ag NMR spectra of the following solid inorganic silver-containing compounds were investigated: $AgNO_3$, $AgNO_2$, Ag_2SO_4, Ag_2SO_3, $AgCO_3$, Ag_3PO_4, AgCl, AgBr, AgI, $AgSO_3CH_3$, silver *p*-toluenesulfonate, $NaAg(CN)_2$, $KAg(CN)_2$, $K_3Ag(CN)_4$, Me_4NAgCl_2, silver diethylthiocarbamate, silver lactate, silver acetate, silver citrate, and bis[(*N*,*N*^{1}-di-*tert*-butylformamidinato)silver(I)]. The magic angle spinning (MAS) spectra of all compounds were obtained. In some cases, when protons were available, the ^{1}H to ^{109}Ag cross-polarization (CP) technique was used to enhance the signal and shorten the experimental relaxation delay. It was possible to obtain slow MAS (or CP/MAS) or nonspinning spectra for 10 samples, allowing the determination of the principal components of the ^{109}Ag chemical shift (CS) tensors. The isotropic chemical shifts and the CS tensors are discussed in light of the available crystal structures. The need for an accepted standard for referencing ^{109}Ag chemical shifts and the use of $AgSO_3CH_3$ as a CP setup sample are also discussed.

Introduction

Two magnetic isotopes of silver exist: ^{107}Ag (51.8%, $I = {}^1/_2$, $\gamma = -1.0828 \times 10^7$ T^{-1} s^{-1}); ^{109}Ag (48.2%, $I = 1/2$, $\gamma = -1.2449 \times 10^7$ T^{-1} s^{-1}). The preferred isotope for NMR spectroscopic observation is ^{109}Ag, due to its slightly higher receptivity. The observation of ^{109}Ag NMR signals has always been a challenge. There are two main reasons for this; both of which are a consequence of the rather low gyromagnetic ratio, γ, for ^{109}Ag. First, the relative receptivity of ^{109}Ag is rather low, at only 28% of that for natural abundance ^{13}C. The NMR receptivity of a spin $^1/_2$ nucleus varies as γ^3.[1] Second, ^{109}Ag generally suffers from extremely long spin−lattice relaxation times, T_1. Heteronuclear dipole−dipole relaxation depends on $\gamma_X{}^2$ and $r_{XH}{}^{-6}$. Since γ_{Ag} is quite small and Ag−H distances are usually rather long, the contributions from this mechanism are usually very small. Furthermore, although ^{109}Ag can have very large chemical shift anisotropies on the ppm scale, the term $(\gamma B_0 \Delta\sigma)^2$ in the chemical shift anisotropy contribution to T_1 is usually quite small. Hence the two most important mechanisms for spin−lattice relaxation for $I = 1/2$ contribute very little to the spin−lattice relaxation of ^{109}Ag. In addition there are instrumental problems associated with the observation of low-frequency nuclei such as ^{109}Ag.[1] Most commercial probes are optimized for observation of higher frequency nuclei, and ^{109}Ag is often at the lower end of the tuning range.

Many of these problems are compounded when one attempts to observe a low-frequency nucleus in the *solid state*. Magic angle spinning spectra usually yield lines which are much broader, thus less intense, than those in solution spectra; splitting of the line shape into spinning sidebands (due to the chemical shift anisotropy) further reduces the observed signal-to-noise ratio. Due to the rigid nature of many solids the mechanisms mentioned above may not contribute yielding relaxation times that are often *much* longer than those in solution. Probe ringing usually makes the observation of a broad “static” line shape for a nonspinning sample practically impossible without the implementation of spin−echo techniques, which further reduces the signal intensity. At present, commercial probes capable of performing ^{109}Ag MAS or CP/MAS experiments must be custom built.

Chemical Shift Tensor. The dominant interaction that affects the line shape in ^{109}Ag NMR spectra is the chemical shift (CS) interaction. The chemical shift interaction can be described by a second rank tensor, and in the principal axis system, the symmetric part of the tensor can be described by three principal components, δ_{11}, δ_{22}, and δ_{33}, such that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. The isotropic chemical shift, which is observed in solution and MAS spectra, is the average of the three principal components of the CS tensor. The CS tensor can be conveniently described by the span, Ω, which reflects the total width of the line shape, and the skew, κ:

$$\Omega = \delta_{11} - \delta_{33} \qquad (1)$$

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[1] Smith, M. E. *Annu. Rep. NMR Spectrosc.* **2000**, *43*, 121.

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$$\kappa = \frac{3(\delta_{22} - \delta_{\mathrm{iso}})}{\Omega} \qquad (2)$$

Review of Previous Work. Due to the reasons discussed above, there have been relatively few solid-state ^{109}Ag NMR studies. Smith has recently reviewed the progress made in the solid-state NMR spectroscopy of low-γ nuclei up to 1999.[1] If one excludes work done on glasses of variable composition, the whole of solid-state silver NMR spectroscopy is contained in 10 reports.[2] The results of these studies are summarized in Table 1. It is surprising how few simple silver salts are included. There are even fewer reports of ^{109}Ag chemical shift anisotropies. To date ^{109}Ag CSA values have been reported for only 3 compounds. The only ^{109}Ag CSA obtained from a static powder spectrum is for crystalline $2AgI{\cdot}Ag_2MoO_4$, which is consistent with $\Omega \approx 70$ ppm and $\kappa = -1$.[2j] Although spinning sideband patterns have been observed in the CP/MAS spectra of several silver compounds, these have not been analyzed to yield the CS tensor parameters. The one study in which this was done estimated chemical shift tensor components for two compounds: $AgS(CH_2)_3CH_3$ and $Ag_5[S(CH_3)_3NMe_3]_3[S(CH_3)_3NHMe_2]_3(ClO_4)_2$.[2b,c]

Experimental Section

The following samples were of commercial origin: $AgNO_3$, Ag_2SO_4, Ag_2SO_3, $AgSO_3CH_3$, Ag_3PO_4, Ag_2CO_3, $KAg(CN)_2$, $NaAg(CN)_2$, AgSCN, Ag_2O, $AgIP(CH_3)_3$, silver diethylthiocarbamate, silver lactate, silver acetate, silver citrate, and silver *p*-toluenesulfonate. The salts AgCN, $AgNO_2$, and $AgPO_3CH_3$ were made as precipitates from mixing aqueous solutions of silver nitrate and the corresponding sodium salts. A sample of $K_3Ag(CN)_4$ was prepared by mixing KCN and AgCN in a 3:1 molar ratio, dissolving the mixture in a minimum amount of water and allowing the solution to evaporate to dryness. Bis[(*N,N*^{1}-di-*tert*-butylformamidinato)silver(I)] was provided by Professor Michael Denk of the University of Guelph Chemistry Department.

All NMR experiments were performed on a Bruker Avance-500 operating at a frequency of 23.27 MHz for ^{109}Ag with a low-frequency (^{109}Ag−^{13}C) 7 mm CP/MAS probe. Magic angle spinning experiments were performed with typical sample spinning rates of 2−4 kHz. The 90° pulse for simple one pulse experiments was 10 μs. The 90° proton pulse, and hence the ^{109}Ag 90° pulse, for CP experiments was set to 8 μs. Cross-polarization experiments used contact times of 40 ms (see refs 3 and 4 for a discussion of this), and a sample of $AgSO_3CH_3$ was used to set up the ^{109}Ag/^{1}H Hartman−Hahn match. The ^{109}Ag chemical shift of solid $AgSO_3CH_3$ is 87.2 ppm with respect to a 9 M aqueous solution of $AgNO_3$.[4]

Table 1. Summary of Previously Determined ^{109}Ag Chemical Shifts in Solids

compd	δ_{iso} (ppm)	ref
$Ag[CH_3CHC(OH)CO_2$, silver lactate	346, 320, 220, 211	2a
$Ag[CH_3CH_2]$, silver acetate	401.2, 382.7	2a
$Ag(CH_3C_6H_4SO_3)$	44.1	2a
$Ag(C_5H_7O_2)$	471.6	2a
$AgN(SO_2Me)_2$	210.3	2a
$AgN(SP_2Me)_20.25H_2O$	182.8, 130.7, 32.5	2a
$Ag_5[(SCH_2)_3NMe_2H)_3](ClO_4)_2$	1228, 826	2b
$[(C_6H_5)_4P]_2[Ag_4(SCH_2C_6H_4CH_2S)_3]6MeOH$	1230, 1220, 1203, 1083	2b
$AgS(CH_2)_3CH_3$ (all trans)	962, 952	2d
$AgS(CH_2)_3CH_3$ (all gauche)	1083, 1048	2a
$((CH_3)_4N)_2[Ag_5(SC_6H_5)_7]$	1141, 980	2b
Ag_2(1,5-pentaethiolate)	900−1300	2b
$[P(C_6H_5)_3Me][AgI_3]$	675	2b
$Ag_5\{\mu_2\text{-}S(CH_2)_3N(CH_3)_2\}_3\{\mu_2\text{-}S(CH_2)_3NH(CH_3)_2\}_3(ClO_4)_2$	1228, 826	2b
AgI	710, 728, 680	2e,f
AgCl	370, 353.5, 409	2e,f
AgBr	350, 350	2e,f
AgF	−110, −125	2e,f
KAg_4I_5	810	2e
$RbAg_4I_5$	790	2e
$Ag_{26}I_{18}W_4O_{16}$	580	2e
Ag_2MoO_4	130	2j
$AgPO_3$	96	2g
$Ag_4P_2O_7$	383	2g
$Ag_{10}Si_4O_{13}$	320	2i
$AgNO_3$	−87	2h
silver metal	−5253	2h

Slow MAS spectra were simulated with the WSOLIDS program, which was kindly provided by the research group of Dr. R. E. Wasylishen.[5]

Results and Discussion

Choice of Primary Reference. The traditional primary reference standard for ^{109}Ag NMR spectroscopy has been an aqueous solution of $AgNO_3$. However the ^{109}Ag chemical shift of aqueous $AgNO_3$ shows a strong dependence on concentration. Unfortunately, many reports of ^{109}Ag shifts do not include the concentration of the standard solution. Solutions of $AgNO_3$ also have the disadvantage of having extremely long ^{109}Ag T_1 values. One report yields a value of 682 s (4 M in H_2O).[6] Figure 1 shows the ^{109}Ag chemical shift for several concentrations of $AgNO_3$ solution. As can be seen the chemical shift increases by about 50 ppm in going from 9 M (nearly saturated) to 1 M concentrations. We propose that 9 M aqueous $AgNO_3$ be consistently used as the primary standard when reporting ^{109}Ag chemical shifts in the future. This sample yields a strong single peak with one pulse. Unfortunately, the very long T_1 makes the determination of the 90° pulse difficult. An alternative for setting pulse lengths is a silver-doped glass, where the silver concentration is high, the spectral line is reasonably narrow, and the T_1 is reasonably short.[7] These samples, however, are not trivial to prepare.

Cross-Polarization from ^{1}H to ^{109}Ag. Using CP to enhance the ^{109}Ag signal can have dramatic effects. The

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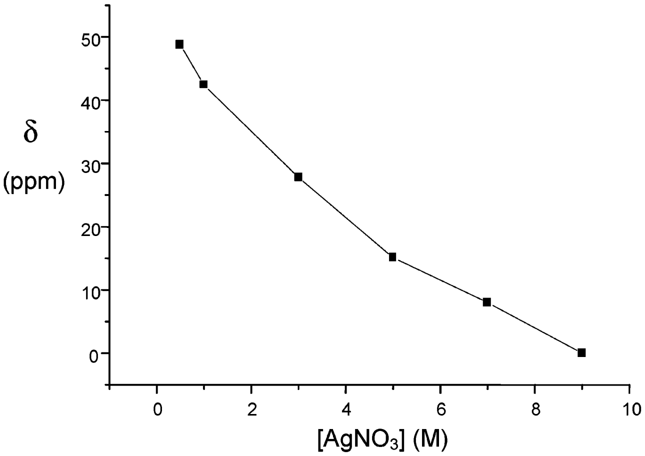

Figure 1. Plot of the relative chemical shift of the ^{109}Ag signal in an aqueous $AgNO_3$ solution as a function of concentration.

potential enhancement factor due to CP is $\gamma(^1H)/\gamma(^{109}Ag) = 21.7$! In practice an enhancement of this magnitude is never realized. Of much more practical importance is the fact that the recycle (relaxation) delay used in CP experiments is dependent on the T_1 of the protons. Proton T_1 values are orders of magnitude shorter than those for ^{109}Ag. This was first demonstrated for the two low-γ nuclei ^{109}Ag and ^{89}Y by Sebald and co-workers.[2a] The practical implication is that with CP one should be able to obtain a multiscan spectrum with excellent S/N in the time it takes to obtain a single pulse spectrum without CP, after allowing for relaxation.

The first step in performing ^{109}Ag CP/MAS experiments is to choose an appropriate sample with which to set up the ^{1}H/^{109}Ag Hartmann−Hahn match. We have shown that $AgSO_3CH_3$ fits nearly all of the criteria as an ideal setup sample and standard and is superior to the previously used silver lactate. A strong single peak is visible after only one pulse, and relaxation delays of only 5 s are needed. The chemical shift of solid $AgSO_3CH_3$ is +87.2 ppm with respect to a 9 M aqueous $AgNO_3$ solution. [3]

Silver Nitrate ($AgNO_3$). A ^{109}Ag MAS spectrum of pure powdered $AgNO_3$ was obtained with a reasonable S/N by allowing the sample to magnetize overnight before applying a single 90° pulse. The chemical shift is −76.0 ppm. This can be compared to a previous report of −87 ppm.[8] The difference may be due to a difference in concentration of the reference sample of aqueous $AgNO_3$. The relaxation delay used by Plischke and co-workers was certainly too short. The chemical shift of aqueous $AgNO_3$ rapidly decreases with increasing concentration of Ag^+. The change in going from 1 to 9 M is −50 ppm. Therefore, it is not surprising that there should be a further shift of −76 ppm in going from 9 M solution to pure $AgNO_3$ (∼25 M). A crude extrapolation of the last 3 points in Figure 1 yields an estimated chemical shift of −65 ppm for 25 M (pure) silver nitrate.

Crystalline $AgNO_3$ is orthorhombic with space group $P2_12_12_1$.[9] There are 2 silver cations/crystallographic asymmetric unit, and these exist in pairs of inequivalent Ag^+ separated by only 3.22 Å. Each silver has 4 additional Ag···Ag interatomic distances of less than 5 Å and 6 Ag···O contacts of less than 3 Å. It is surprising that only one peak is observed in the ^{109}Ag MAS spectrum since the two crystallographically inequivalent silver ions have quite different contacts with nearby Ag and O atoms. It is possible that the two silver nuclei happen to be in nearly identical magnetic environments. It is also possible that one silver nucleus has a spin−lattice relaxation time that is so long that it is not sufficiently magnetized in this experiment. Another explanation for the absence of a second signal after a single scan is that either ^{109}Ag resonance is too broad or that the chemical shift anisotropy is so large that the signal is spread out over many spinning sidebands. A less likely scenario is that the silver cations are rapidly diffusing within the crystal lattice, yielding a single, averaged, peak. The absence of spinning sidebands indicates that the Ω value for the observable ^{109}Ag in solid $AgNO_3$ is less than about 20 ppm.

Silver Nitrite ($AgNO_2$). There have been three investigations of the crystal structure of silver nitrite.[10] The first structure gave an Ag−N distance of 2.07 Å, implying significant covalent bonding.[10a] The most recent structure yields a distance of 2.304 Å,[10c] which is still indicative of some covalent character between Ag and N. The structure is arranged in such a way that there are two $AgNO_2$/unit cell. Each silver atom is surrounded by a nitrogen at 2.304(2) Å, two oxygen atoms from a nearby NO_2 anion, and four more oxygen atoms at 2.722(2) Å, each from a different nitrite anion. The ^{109}Ag chemical shift in solid $AgNO_2$ is 84.9(2) ppm. This represents a deshielding of 161 ppm with respect to that of solid $AgNO_3$.

Silver Sulfate (Ag_2SO_4). Ag_2SO_4 crystallizes in the orthorhombic space group *Fddd* with $Z = 8$.[11] The structure of solid Ag_2SO_4 (not shown) indicates that each Ag is surrounded by six oxygen atoms with pairs of Ag−O distances of 2.41, 2.43, and 2.69 Å and that the shape of the AgO_6 polyhedron corresponds to a distorted trigonal prism. The structure also shows that the Ag cations are related by centers of inversion and thus are chemically and magnetically equivalent. This is in accordance with the ^{109}Ag MAS spectrum, which consists of one single narrow peak (not shown).

Silver Sulfite (Ag_2SO_3). As described by Larsson, solid Ag_2SO_3 exists in the space group $P2_1/c$ with two chemically inequivalent Ag atoms in the crystallographic asymmetric unit.[12] One Ag atom is coordinated to three oxygen atoms from three different SO_3 groups and one sulfur atom in an approximately tetrahedral arrangement. The other Ag is coordinated to four oxygen atoms in a very distorted

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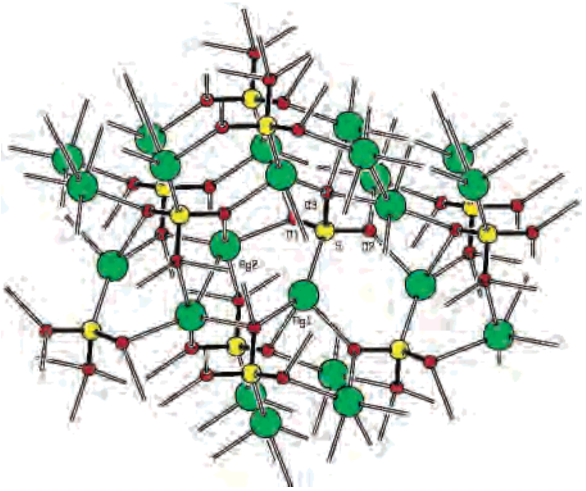

Figure 2. Crystal structure of silver sulfite.

tetrahedral arrangement. Figure 2 shows the two Ag atoms and their coordination to nearby oxygen and sulfur atoms. There are no close Ag−Ag contacts. This structure implies that one should see two signals in the ^{109}Ag MAS spectrum. This is indeed the case, as shown in Figure 3. The chemical shifts for the two silver atoms are 466.1 and 475.6 ppm. The spans of the ^{109}Ag CS tensors are estimated from simulations to be 895 and 785 ppm, respectively. At present it is not possible to assign the two resonances to the two inequivalent silver nuclei.

Silver Methanesulfonate ($AgCH_3SO_3$). The crystal structure of $AgSO_3CH_3$ indicates that there are 4 chemically equivalent silver ions in the unit cell and each Ag atom is surrounded by five oxygen atoms, each from a different $SO_3CH_3^-$ anion.[13] The arrangement of the oxygen atoms around the silver is a distorted trigonal bipyramid. The sixth position is held by a more distant silver (Ag−Ag distance of 3.163(2) Å). As mentioned earlier, the ^{109}Ag CP/MAS spectrum of silver methanesufonate is quite strong and has been suggested as a reference for performing ^{109}Ag CP/MAS experiments. The good signal-to-noise for this sample makes it possible to obtain a powder spectrum of the nonspinning sample with CP. The CP/MAS and nonspinning CP spectra can be found in ref 4. Analysis of the powder spectrum gave $\Omega = 183.4(5)$ ppm and $\kappa = 0.53(1)$. This is consistent with the arrangement of the oxygen atoms around the silver.

Silver *p*-Toluenesulfonate (Ag−pTS). When the first ^{109}Ag CP/MAS experiments were performed a decade ago one of the compounds investigated was Ag−pTS.[2a] At that time no crystal structure was available. Since then two crystal structure reports for Ag−pTS have appeared.[14] Solid Ag−pTS exists in a monoclinic phase with space group $P2_1/a$. There are two silver atoms/unit cell, and these are related by a center of inversion. Therefore, the two corresponding ^{109}Ag nuclei are chemically and magnetically equivalent. Ag−pTS is a layered compound, much like many of the metal phosphonates, with an interlayer spacing of 15.309(1) Å. The Ag^+ ion in Ag−pTS is unusual in that there are 7 other atoms within the sum of van der Waals distances. Two of these are silver atoms and five are sulfonate oxygen atoms.

Our CP/MAS spectrum (Figure 4a) yields a δ value of 46.1(2) ppm, quite close to that of Seebald and Merwin.[2a] The good S/N for this sample allowed us to obtain a static spectrum (Figure 4b). The CS tensor components are $\delta_{11} = 114(2)$ ppm, $\delta_{22} = 54(2)$ ppm, and $\delta_{33} = -49(2)$ ppm to give $\Omega = 217(4)$ ppm and $\kappa = 0.11(1)$.

Silver Phosphate (Ag_3PO_4). The crystalline structure of Ag_3PO_4 is cubic with space group $P\bar{4}3n$ and $Z = 2$.[15] The regular PO_4 tetrahedra, with a P−O distance of 1.539 Å, form a body-centered cubic lattice. The six Ag^+ ions are disordered among 12 sites with 2-fold symmetry. Each Ag^+

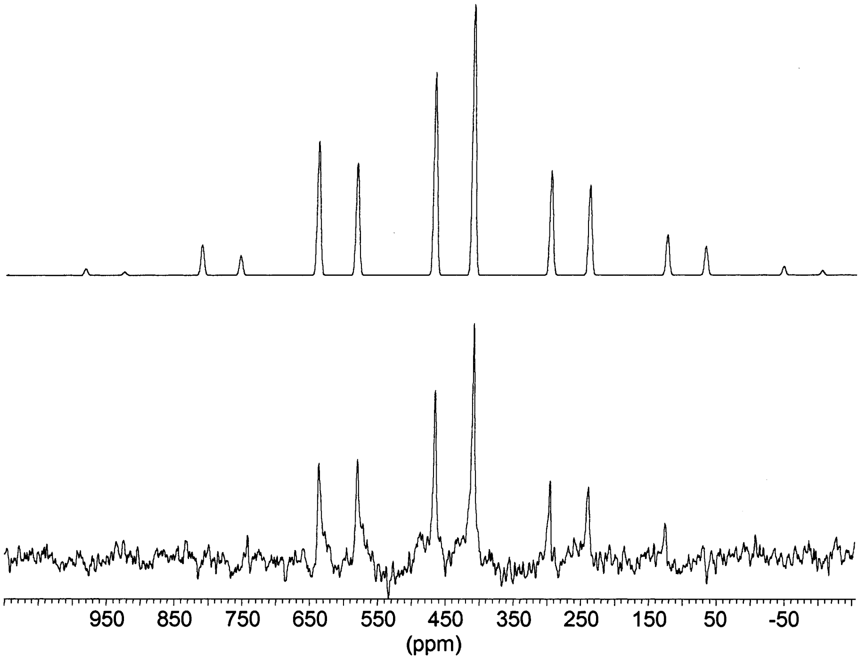

Figure 3. ^{109}Ag MAS spectrum and simulation for solid silver sulfite. This spectrum was obtained with a relaxation delay of 12 h and required 8 days of spectrometer time.

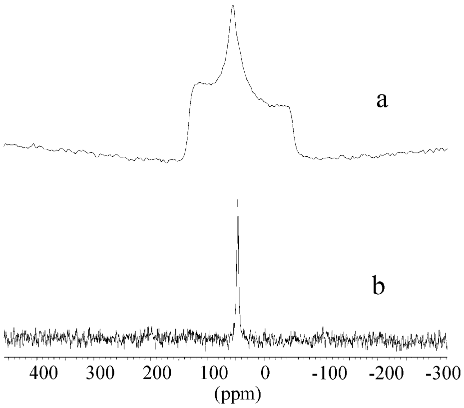

Figure 4. ^{109}Ag CP spectrum of solid silver *p*-toluenesulfonate: (a) without sample spinning; (b) with MAS at 3 kHz.

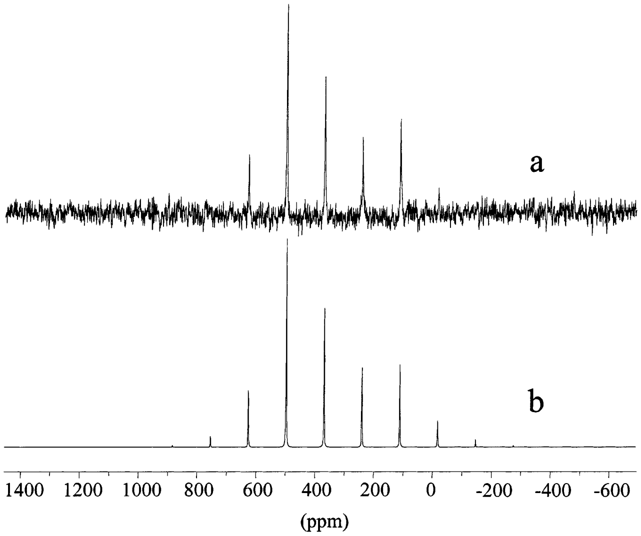

Figure 5. (a) ^{109}Ag MAS spectrum of solid silver carbonate and (b) simulated spectrum.

occupies one of two possible sites on either side of the ideal site so that its symmetry is lowered from 4-fold to 2-fold. The Ag^+ is coordinated to four oxygen atoms, belonging to four different phosphate groups, to form an irregular tetrahedron. Each oxygen is, in turn, bonded to three Ag^+ ions. The closest Ag−Ag contact is 2.77 Å. The MAS spectrum yields a single peak at 342.5 ppm.

Silver Carbonate (Ag_2CO_3). The ^{109}Ag MAS spectrum of Ag_2CO_3 is shown in Figure 5a. The ^{109}Ag T_1 in Ag_2CO_3 was obviously shorter than that in $AgNO_3$, Ag_2SO_3, or Ag_2SO_4. This allowed us to obtain an MAS spectrum with 16 scans (recycle delay of 4000 s). The MAS spectrum clearly shows a pattern of spinning sidebands due to CSA, and a simulation of the spinning sideband pattern (also shown in Figure 5b) yields a CS tensor with a fairly large span, Ω, of 711(10) ppm and skew, κ, of 0.36(2). Crystalline Ag_2CO_3 is monoclinic and belongs to the space group $P2_1/m$ with $Z = 2$.[16] The two silver atoms are chemically equivalent, which is consistent with the single isotropic chemical shift at 369.8(1) ppm measured for solid Ag_2CO_3. The crystal structure indicates that each Ag has a total of 8 other atoms within the sum of the van der Waals distances (see Figure 6). It is difficult to say why the ^{109}Ag CSA is so large, but it may have something to do with the two rather close Ag−Ag contacts of 3.124 and 3.284(2) Å. These are significantly shorter than the van der Waals contact distance of 3.52 Å.

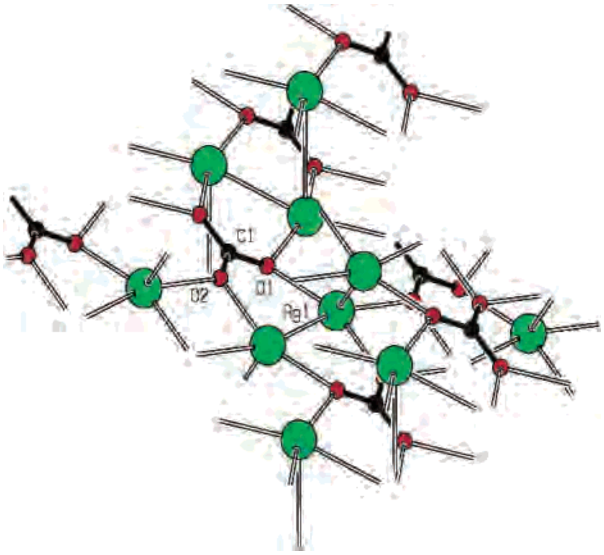

Figure 6. Crystal structure of silver carbonate.

Carboxylic Acid Salts of Silver. The CP/MAS spectra salts silver lactate, silver acetate, and silver acetylacetonate have been reported by Merwin and Sebald.[2a] Our measurements for silver lactate and silver acetate are in good agreement with their work. In addition we looked at the commercially available citrate salt. The ^{109}Ag shift of 95.7 ppm is quite different from the other 3 carboxylic acid salts. Evidently the coordination around the silver in silver citrate is quite different from that of the acetate or lactate. The observation of a single spectral peak suggests that the three silver sites in $Ag_3C_6H_5O_7$ are all equivalent or very nearly equivalent. Unfortunately, crystal structures are not available for any of these silver salts. It is therefore rather difficult to discuss these salts in much more detail.

Silver Halides. There are several reports of ^{109}Ag NMR investigations of the silver halides.[17,18] This represents the first MAS study of AgCl, AgBr, and AgI. The chemical shifts in silver halides show considerable sensitivity to the halide counterion as has been reported for other metal halides.[19] Silver iodide has been of central importance to silver-based fast ion conducting phases and glasses, and it displays significant polytypism, with the isotropic chemical shift of the polytypes covering a range of 100 ppm.[20] Our measure-

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Table 2. ^{109}Ag NMR Chemical Shifts of Silver Halides, Including Previous Work

	^{109}Ag δ (ppm) at room temperature		
solids	ref 17[a]	ref 18[b]	this work[c]
AgCl	370 (417)	-3.5 ± 0.5 (423.8)	423.4
AgBr	350 (397)	0 (420.3)	420.3
AgI	710 (757)	-330 ± 3 (753.4)	757.0, 780.6

[a] The chemical shift reference is aqueous 9.1 M $AgNO_3$ + 0.24 M $Fe(NO_3)_3$. The numbers in parentheses are the values after shifting by 47 ppm. [b] The chemical shift with respect to solid AgBr. The numbers in parentheses are the values after changing the sign of δ and adding 420.3 ppm. [c] The chemical shift reference is aqueous 9.0 M $AgNO_3$. The uncertainty in each value is estimated to be ±1 ppm.

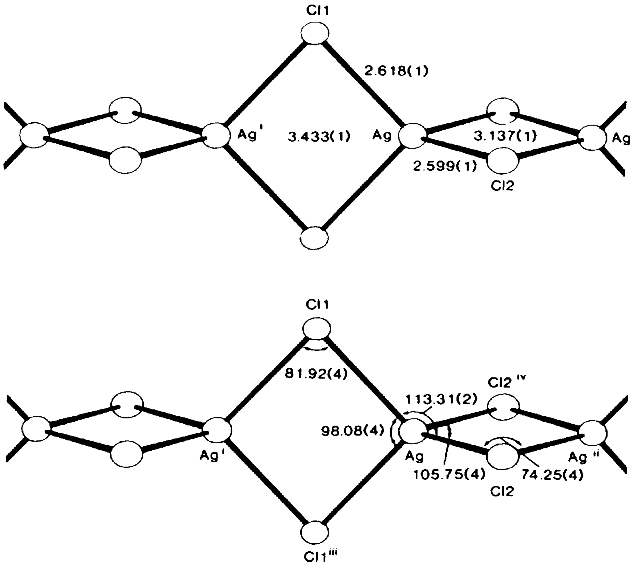

Figure 7. Structure of solid $N(CH_3)_4AgCl_2$.

ments are in good agreement with those of Becker and von Goldammer[17] but show poorer agreement with those of Looser and Brinkmann.[18] Our results, together with those of Becker and von Goldammer and Looser and Brinkmann (corrected for differing reference samples), are shown in Table 2. Two peaks are observed for solid AgI, corresponding to two different polytypes. These peaks were also observed by Becker and von Goldammer.[17] A detailed discussion of the ^{109}Ag, ^{35}Cl, ^{81}Br, and ^{19}F spectra of silver halides can be found elsewhere.[17]

Tetramethylammonium *catena*-Bis(μ-chloro)argentate(I) [$(CH_3)_4NAgCl_2$]. The crystal lattice of $(CH_3)_4NAgCl_2$ consists of chains of $AgCl_2$ units as shown in Figure 7.[21] Each pair of Ag atoms is bridged by a pair of Cl atoms. The Ag atoms are the centers of rather distorted tetrahedra, and the symmetry at each Ag is C_{2v}. The Ag atoms are related by centers of inversion and are therefore chemically and magnetically equivalent to yield one ^{109}Ag resonance. This is consistent with the observed CP/MAS spectrum, which is shown in Figure 8a. The spectrum of a nonspinning sample is shown in Figure 8b. The small skew of the CS tensor is consistent with the low symmetry around the silver atom.

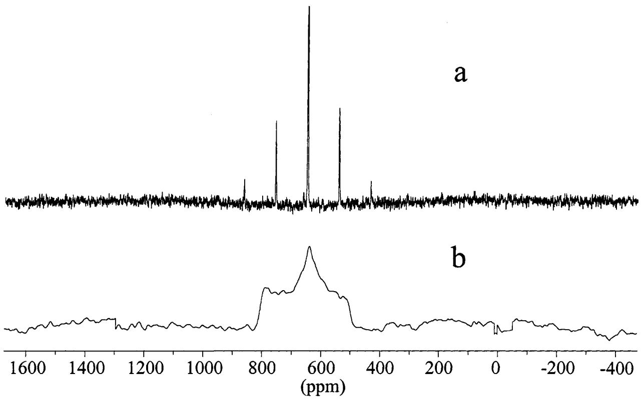

Figure 8. (a) ^{109}Ag CP/MAS spectrum and (b) nonspinning CP spectrum of solid $N(CH_3)_4AgCl_2$.

Silver Cyanide and Argentate Salts. Silver cyanide represents one of the few simple inorganic salts whose structures are still not known in detail. The structure of solid AgCN was studied fairly recently by Bowmaker et al.[22] Their neutron diffraction investigation shows that solid AgCN exists as infinite linear chains of alternating silver and cyanide ions. One aspect of the structure that was not considered was that of head-to-tail disorder of the cyanide anion. In the past year two studies published in *Inorganic Chemistry* have addressed this question. Hibble et al. undertook a total neutron diffraction investigation into the structure of solid AgCN in which they took random disorder into account.[23] A recent ^{15}N and ^{13}C solid-state NMR study by Bryce and Wasylishen estimates that 30% of the silver sites have −NC−Ag−CN− versus −CN−Ag−NC− disorder and about 70% are ordered as −NC−Ag−NC− units.[24] In principle ^{109}Ag MAS experiments should be ideally suited for investigating the head-to-tail disorder in solid AgCN. Unfortunately, the ^{109}Ag T_1 is extremely long and the chemical shift anisotropy is so large that no signal could be detected, even after 4 scans with a relaxation delay of 24 h!

Silver forms three simple argentate anions with cyanide: $Ag(CN)_2^-$; $Ag(CN)_3^{2-}$; $Ag(CN)_4^{3-}$. The structure of solid $NaAg(CN)_2$ (Figure 9) is made up of layers of linear NC−Ag−CN$^-$ anions, with Na ions occupying octahedral holes between the nitrogen layers.[25] The experimental and simulated ^{109}Ag MAS spectra of $NaAg(CN)_2$ are shown in Figure 10. The isotropic chemical shift is 636.7 ppm. The axial symmetry of the ^{109}Ag CS tensor ($\kappa = +1$) is consistent with a linear environment about the Ag atom and with the fact that the Ag atom lies on a crystallographic inversion center. The tensor also has a large span (Ω = 1720 ppm). A very

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(19) (a) Becker, K. D. *Chem. Phys.* **1980**, *48*, 193. (b) Becker, A. D.; Schäfgen, H. P. *Solid State Commun.* **1979**, *32*, 1107. (c) Nizam, M.; Allavena, M.; Bouteiller, Y.; Suits, B. H.; White, D. *J. Magn. Reson.* **1989**, *82*, 441. (d) Nolle, A. *Z. Naturforsch.* **1978**, *33A*, 666.

(20) See, for example: (a) Villa, M.; Chiodelli, G.; Magistris, A.; Licheri, G. *J. Chem. Phys.* **1986**, *85*, 2392. (b) Mustarelli, P.; Tomasi, C.; Magistris, A.; Cutroni, M.; Mandanici, A. *Phys. Rev.* **1998**, *B58*, 9054.

(21) Helgesson, G.; Josefsson, M.; Jagner, S. *Acta Crystallogr.* **1988**, *C44*, 1729.

(22) Bowmaker, G. A.; Kennedy, B. J.; Ried, J. C. *Inorg. Chem.* **1998**, *37*, 3968.

(23) Hibble, S. J.; Cheyne, S. M.; Hannon, A. C.; Eversfield, S. G. *Inorg. Chem.* **2002**, *41*, 1042.

(24) Bryce, D. L.; Wasylishen, R. E. *Inorg. Chem.* **2002**, *41*, 4131.

(25) Range, K.-J.; Kühnel, S.; Zabel, M. *Acta Crystallogr.* **1989**, *C45*, 1419.

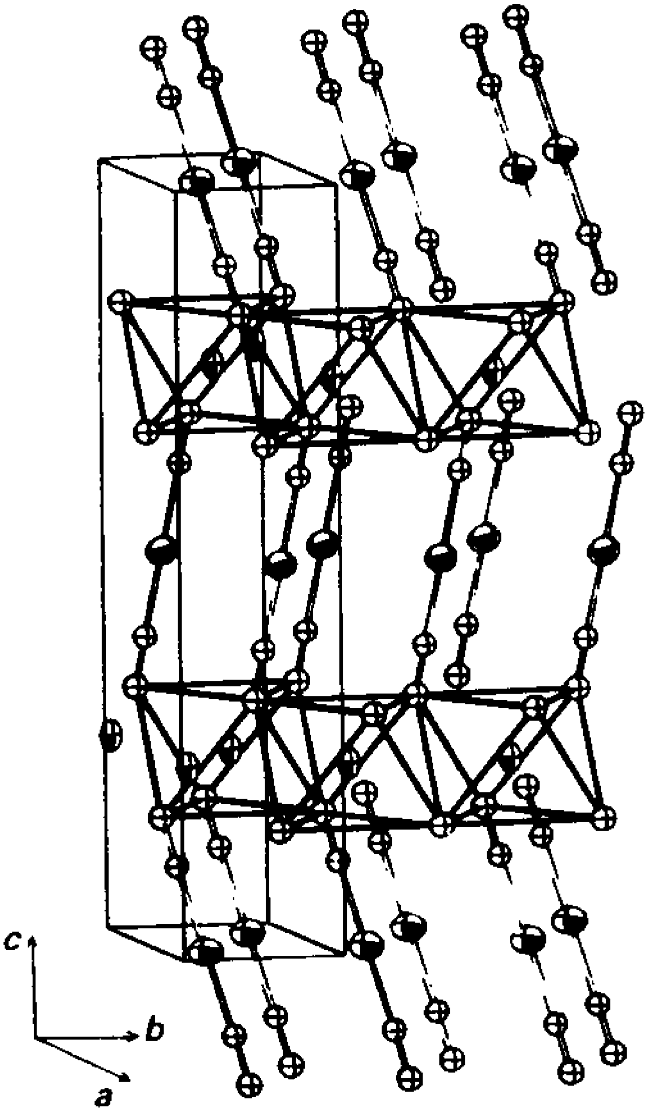

Figure 9. Crystal structure of solid $NaAg(CN)_2$.

early study of the system $KCN-AgCN-H_2O$ showed the existence of the compounds $KAg(CN)_2$, $K[Ag_2(CN)_3]\cdot H_2O$, and $K_3[Ag(CN)_4\cdot H_2O$.[26] At present, only the structure of $KAg(CN)_2$ is known in detail.[27,28] This structure (shown in Figure 11a) is quite different from that of solid $NaAg(CN)_2$. The unit cell is trigonal, with $Z = 2$ and one $Ag(CN)_2$ anion/crystallographic asymmetric unit, forming alternate layers of K^+ ions and linear $Ag(CN)_2$ ions. Whereas there are no close Ag−Na contacts in solid $NaAg(CN)_2$, the closest distance between K and Ag in $KAg(CN)_2$ is 3.831 Å. This is considerably smaller than the sum of van der Waals radii (4.47 Å). The ^{109}Ag MAS spectrum of $KAg(CN)_2$ is shown in Figure 11b. The isotropic chemical shift of 831.7(2) ppm shows a deshielding of 195 ppm with respect to $NaAg(CN)_2$. The span of the CS tensor is 1375(10) ppm, 345 ppm smaller than that in $NaAg(CN)_2$. These differences are extremely large considering that the structures of the dicyanoargentate anions in the two compounds are nearly identical and are likely due to the close K−Ag contacts in the potassium salt. The silver atom of $KAg(CN)_2$ sits on a crystallographic inversion center. This is consistent with a κ value of $+1$.

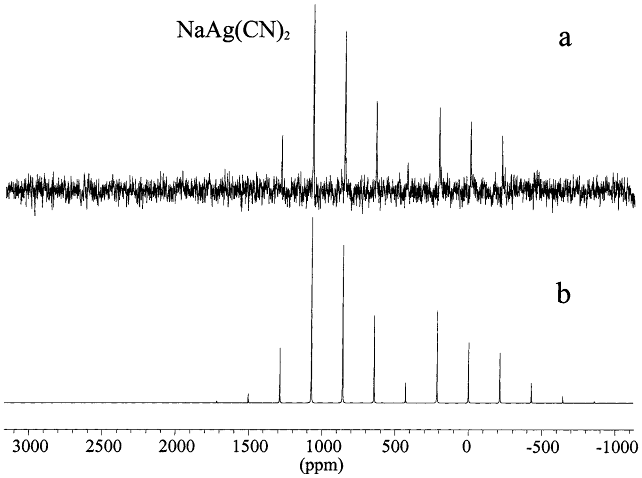

Figure 10. (a) ^{109}Ag MAS spectrum of solid $NaAg(CN)_2$ and (b) simulated MAS spectrum of solid $NaAg(CN)_2$.

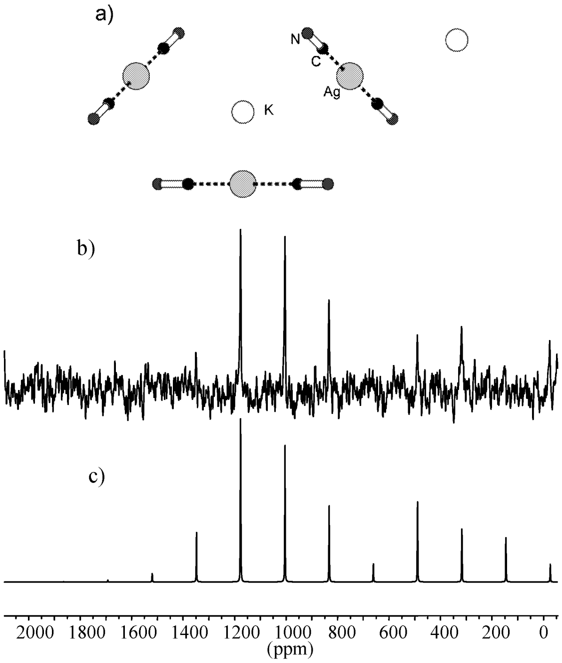

Figure 11. (a) Structure of solid $KAg(CN)_2$, (b) ^{109}Ag MAS spectrum of solid $KAg(CN)_2$, and (c) simulated ^{109}Ag MAS spectrum of solid $KAg(CN)_2$.

Another argentate anion that can be isolated from the $KCN-AgCN-H_2O$ system is $K_3[Ag(CN)_4]\cdot H_2O$, although it was later proposed that the formula should be $K_3[Ag(CN)_4]$.[29] Powder diffraction studies show that $K_3[Ag(CN)_4]$ is isomorphous with $K_3[Cu(CN)_4]$, which has a trigonal cell with space group $R32$ and $Z = 2$. The symmetric tetrahedral structure of the tetracyanoargentate anion is reflected in the very narrow peak, with no spinning sidebands, obtained in the ^{109}Ag MAS spectrum (not shown). The chemical shift is 1428 ppm. Endo et al. observed the ^{109}Ag spectrum of an aqueous mixture of 1 M $AgNO_3$ and 6 M KCN and predicted

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[26] Bassett, H.; Corbet, A. S. *J. Chem. Soc.* **1924**, *125*, 1660.
[27] Hoard, J. L. *Z. Kristallogr.* **1933**, *A84*, 231.
[28] Staritzky, E. *Anal. Chem.* **1956**, *28*, 419.
[29] Staritzky, E. *Anal. Chem.* **1956**, *28*, 423.

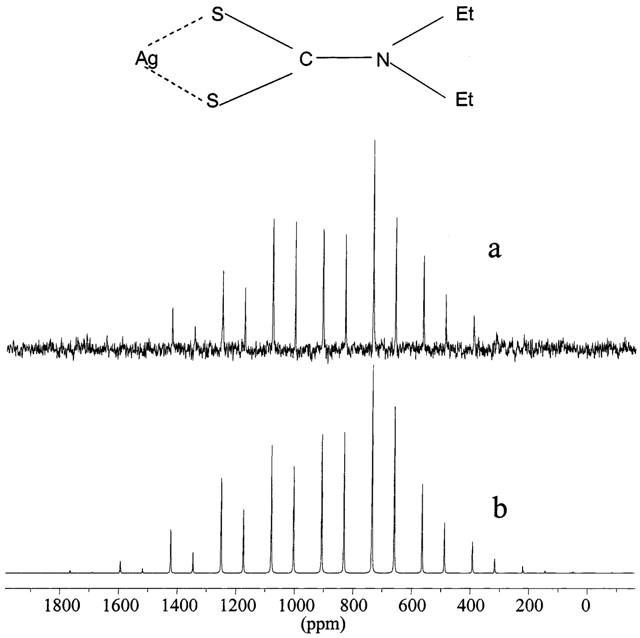

Figure 12. (a) Experimental and (b) simulated ^{109}Ag CP/MAS spectrum of solid silver diethylthiocarbamate.

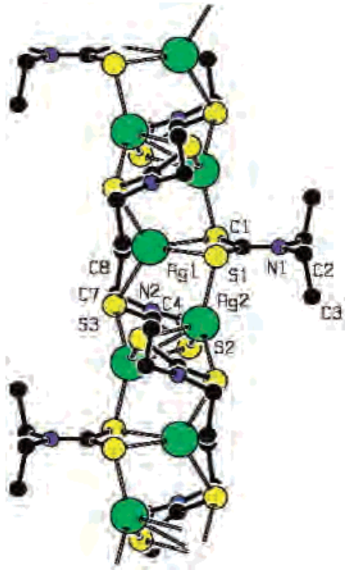

Figure 13. Crystal structure of silver diethylthiocarbamate.

the ^{109}Ag chemical shift of $Ag(CN)_4{}^{3-}$ should be 1224 ppm in solution.[30] It is possible that the gap between these two values would be reduced if the equilibrium in solution were pushed further by increasing the concentration of KCN. Attempts to obtain CP/MAS spectra of the solid failed, in agreement with the suggestion that the compound is not hydrated.

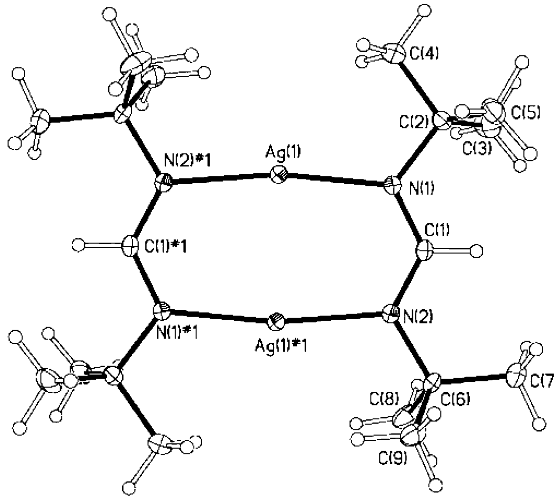

Figure 14. Crystal structure of bis[(*N*,*N*^{1}-di-*tert*-butylformamidinato)silver(I)].

Table 3. Isotropic ^{109}Ag Chemical Shifts in Various Solids

name of silver compd	δ (ppm) (with ref to 9 M $AgNO_3$)
solid $AgNO_3$	-76.0 ± 0.5
$AgNO_2$	84.9 ± 0.5
Ag_2SO_4	52.7 ± 0.5
Ag_2SO_3 (2 sites)	466.1 ± 0.5
	409.5 ± 0.5
$AgSO_3CH_3$	87.2 ± 0.5
Ag-*p*-toluene-SO_3	46.1 ± 0.5
Ag_3PO_4	342.5 ± 0.5
Ag_2CO_3	369.8 ± 0.5
$KAg(CN)_2$	831.7 ± 0.5
$K_3Ag(CN)_4$	1428.4 ± 0.5
$NaAg(CN)_2$	636.7 ± 0.5
Me_4NagCl_2	649.5 ± 0.5
$[AgN_2CCH_3]_2$	692.7 ± 0.5
AgS_2CNEt_2 (2 sites)	906.0 ± 0.5
	836.0 ± 0.5
Ag lactate	327 ± 4
Ag acetate	372 ± 4
Ag citrate	96 ± 4

Silver Diethylthiocarbamate (AgS_2CNEt_2). The ^{109}Ag CP/MAS spectrum of solid AgS_2CNEt_2 is shown in Figure 12. The spectrum consists of two sets of peaks and could only be simulated if two sites in a ratio of 2:1 was assumed. AgS_2CNEt_2 crystallizes in the *C*2/*c* space group with 12 molecules/unit cell.[31] The crystal structure indicates that there are two chemically different Ag atoms, Ag1 and Ag2, in a ratio of 1:2, in perfect accord with the CP/MAS spectrum. The structure shows that alternating AgS_2CNEt_2 and $(AgS_2CNEt_2)_2$ units form helical chains with the CN bonds pointing perpendicular to the axis of the helix. See Figure 13. Ag1 is coordinated to the two sulfurs of the S_2CNEt_2 group and to one sulfur each of the $(AgS_2CNEt_2)_2$ units above and below it. Ag2 is coordinated to the four sulfurs of the two AgS_2CNEt_2 groups, to the other Ag2 in the $(AgS_2CNEt_2)_2$ dimeric unit, and to one sulfur from the AgS_2CNEt_2 units above or below it. Therefore, the two silver atoms are quite different in that Ag1 is coordinated to 4 sulfurs and Ag2 is coordinated to 6 sulfurs and another Ag2. The isotropic chemical shift of Ag2 is 76 ppm higher and the span of the CS tensor is 168 ppm larger than those of Ag1.

Bis[(*N*,*N*^{1}-di-*tert*-butylformamidinato)silver(I)]. The crystal structure of bis[(*N*,*N*^{1}-di-*tert*-butylformamidinato)silver(I)] is shown in Figure 14.[32] Each silver in the unit cell is bonded to two nitrogens, with N−Ag−N angles of 179°.

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(30) Endo, K.; Yamamoto, K.; Matsushita, K.; Deguchi, K.; Kanda, K.; Nakatsuji, H. *J. Magn. Reson.* **1985**, *65*, 268.

(31) Anancker-Eickhoff, H.; Hesse, R.; Jennische, P.; Wahlberg, A. *Acta Chem. Scand.* **1982**, *36A*, 251.

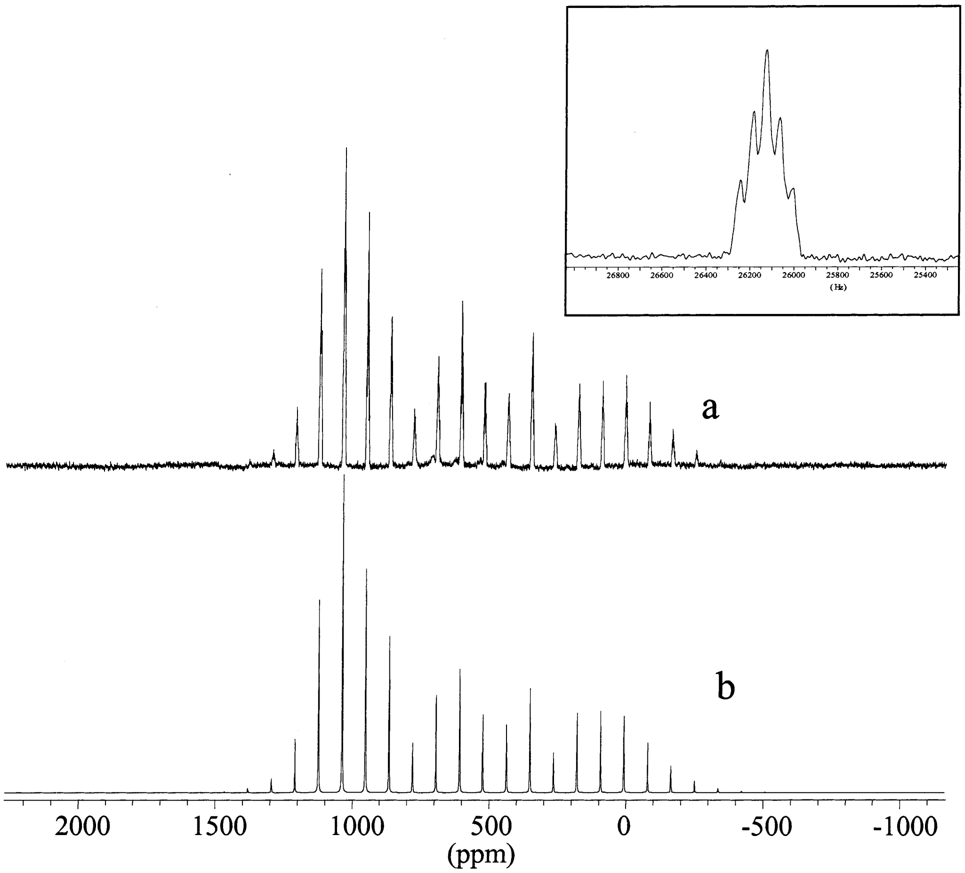

Figure 15. (a) Experimental and (b) simulated ^{109}Ag CP/MAS spectrum of solid bis[(*N*,*N*^{1}-di-*tert*-butylformamidinato)silver(I)]. The inset shows the multiplet structure of the center band.

Table 4. ^{109}Ag Chemical Shift Tensors[a]

name of silver compd	isotropic δ	δ_{11}	δ_{22}	δ_{33}	span Ω	skew κ
Ag_2CO_3	369.8(0.5)	656(5)	502(5)	−55(5)	711	0.56
Ag_2SO_3	466.1(0.5)	827(10)	513(10)	63(10)	764	0.13
	409.5(0.5)	745(10)	445(10)	40(10)	785	0.14
$NaAg(CN)_2$	636.7(0.5)	1210(5)	1210(5)	−510(5)	1720	1.00
$KAg(CN)_2$	831.7(0.5)	1290(10)	1290(10)	−85(10)	1375	1.00
AgS_2CNEt_2 (2 sites)	906.0(0.5)	1508(5)	820(5)	390(5)	1118	−0.23
	830.0(0.5)	1345(5)	750(5)	395(5)	950	−0.25
Me_4NAgCl_2	649.5(0.5)	790(2)	641(2)	517(2)	272	−0.10
$[AgN_2C(CH_3)_3]_2$	692.7(0.5)	1140(5)	1140(5)	−202(5)	1342	1.00
$AgCH_3SO_3$	87.2(0.5)	191(2)	63(2)	8(2)	183	−0.39
Ag-*p*-toluene-SO_3	46.1(0.5)	114(2)	54(2)	−49(2)	163	0.15

[a] Uncertainties are in parentheses.

The two silver atoms are related by a center of inversion, making them chemically and magnetically equivalent. The ^{109}Ag CP/MAS spectrum of bis[(*N*,*N*^{1}-di-*tert*-butylformamidinato)silver(I)], together with a simulation of the spinning sideband pattern, is shown in Figure 15. The chemical shift is 692.7(2) ppm. The Ω and κ values of the CS tensor are 1342(10) ppm and 1.00(5), respectively. The κ value is consistent with the nearly linear N−Ag−N. By far the most interesting feature of the spectrum is the splitting fine-structure observed in the centerband and spinning sidebands. The 1:2:3:2:1 multiplet indicates that each ^{109}Ag is spin−spin coupled to two ^{14}N nuclei. The $^1J(^{109}\mathrm{Ag},^{14}\mathrm{N})$ value is ±58.6(5) Hz. This is the first report of an Ag−N spin−spin coupling in a solid. The fact that $^1J(^{109}\mathrm{Ag},^{14}\mathrm{N})$ could be observed implies a slowly relaxing ^{14}N nucleus, likely the result of a relatively small nuclear quadrupolar coupling constant, $\chi(^{14}\mathrm{N})$.

Samples for Which No ^{109}Ag Signal Could Be Obtained: AgCN and Ag_2O. It is important to indicate which samples yielded no ^{109}Ag signal. As mentioned above, we were unable to obtain a ^{109}Ag MAS spectrum of solid AgCN. Silver oxide (Ag_2O) is one of the simplest silver salts and has the highest concentration by weight of any stable silver salt (96%). Yet several attempts to get a ^{109}Ag MAS spectrum failed. This was very likely a result of a combination of extremely long relaxation times and large (>1000 ppm) chemical shift anisotropies.

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(32) Denk, M. K.; Fournier-Bidoz, S.; Niyogi, D.; Lough, A.; Penner, G. H. Structure deposited with the Cambridge Crystallographic Data Centre, CCDC No. 209653.

Conclusions

The isotropic ^{109}Ag chemical shifts for 20 inorganic silver salts were measured by MAS and CP/MAS NMR spectroscopy. Of these, 15 have not been previously measured. In addition, the principal components of the ^{109}Ag CS tensor for 10 of these samples are presented. None of these values have been previously reported and represent the vast majority of silver CS tensor measurements currently available. Our measurements of ^{109}Ag chemical shifts and principal components of chemical shift tensors are summarized in Tables 2−4. The isotropic chemical shifts and the components of the CS tensor are obviously very sensitive to the environment about the silver nucleus. The crystal structures of the oxy acid salts of silver reveal a wide range of coordination to oxygen and other atoms (such as N and S). Therefore, it is very difficult, at present, to make any wide-ranging statements about the relationship between the ^{109}Ag chemical shift (tensor) and silver coordination. Good high-level molecular orbital calculations, with relativistic corrections, would go a long way toward making more definitive connections between the CS tensor and the coordination of the silver atom in these and other simple silver salts. Nevertheless, we have speculated on some of the differences in the CS tensors between related salts in the previous section.

Acknowledgment. This work was supported by funds from the Natural Sciences and Engineering Research Council (NSERC) of Canada. The Canadian Foundation for Innovation (CFI) and the Ontario Research and Development Challenge Fund (ORDCF) are thanked for providing funds for the purchase of the 500 MHz spectrometer and low-frequency probe. Professor Michael Denk (University of Guelph) kindly provided a sample of bis[(N,N^1-di-*tert*-butylformamidinato)silver(I)]. We furthermore thank Professor Denk for very useful and encouraging comments.

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