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Structural Studies of Organic Silver Complexes in Dimethyl Sulfoxide by ^{13}C and ^{109}Ag NMR

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Abstract: The effects on ^{13}C and ^{109}Ag chemical shifts of complexation of ethylenethiourea, thiazolidine-2-thione, 3-methylthiazolidine-2-thione, dipropylamine, pentamethylene sulfide, and 2-aminothiazole with silver nitrate in dimethyl sulfoxide solution have been examined. Although complexation is reflected via ^{109}Ag chemical shifts of hundreds of parts per million, as compared with only a few parts per million of ligand ^{13}C chemical shifts, both types of NMR data suggest that ligands which bind Ag(I) through sulfur form solutions containing a variety of complex species. By contrast, nitrogen ligands appear to form primarily 2:1 silver-to-ligand complexes. The ^{13}C chemical-shift changes in the unsaturated compounds are discussed in terms of contributions from resonance forms containing different degrees of C=S and C=N bonding in the silver complexes compared to the free ligands.

Introduction

We have shown in an earlier report[1] that a combination of ^{13}C and ^{109}Ag NMR holds promise for determining various structural parameters of organic silver complexes in solution. However, experimental data were obtained only for thiourea and tetramethylthiourea. The apparent structural diversity of the silver-complex systems for these compounds precluded detailed conclusions. Toward a long-term goal of providing a data base which may allow more of the information contained in the ^{13}C and ^{109}Ag spectra of silver complexes to be extracted, we have extended our study to include additional compounds.

The ^{13}C spectra of silver complexes may be useful in providing insight into the effects of complexing of metal ions in general on the ^{13}C chemical shifts of organic ligands. Diamagnetic metal complexes have already been studied. Metal complexes of olefinic and aromatic ligands[2,3] and the shifts caused by metal complexation in carbonyl[4,5] and thiocarbonyl[6,7] compounds have also been studied. A few investigations

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have involved other organic species such as alcohols.[8,9] Many metals were included in these studies, a number of which concerned silver(I) complexes.[3,5,7,9]

Experimental Section

Materials. Most of the compounds used were commercially available, as follows: ethylenethiourea (**1**) (Aldrich, 2-imidazolidinethione); thiazolidine-2-thione (**2**) (Aldrich, 2-mercaptothiazoline); dipropylamine (**4**) (Eastman); pentamethylene sulfide (**5**) (Aldrich); 2-aminothiazole (**6**) (Eastman); 2-amino-2-thiazoline (**10**) (Eastman and Aldrich); rhodanine (Eastman); silver nitrate (Eastman); dimethyl-d_6 sulfoxide (Stohler). In general, the materials were used as received, but the sample of **10** (Aldrich) for the ^{109}Ag spectra, which appeared inhomogeneous, was recrystallized from ethanol.

3-Methylthiazolidine-2-thione (3). This compound was prepared at Kodak under the direction of Mr. M. J. Spitulnik according to the following procedure. Thiazolidine-2-thione was methylated with methyl *p*-toluenesulfonate in the presence of base to give 2-methylthio-3-methyl-2-thiazoline *p*-toluenesulfonate. To a solution of 48 g of sodium sulfide in 50 mL of water was added slowly 32 g of the salt in 50 mL of water while the temperature of the reaction was maintained at 10 °C in an ice bath. A white, crystalline solid precipitated. The reaction mixture was chilled overnight, and the solid was collected by filtration, then washed with water. A further recrystallization from benzene-petroleum ether afforded long, colorless needles, mp 68 °C (lit.[12] 69 °C). Final yield was 10.5 g (79%) based on the 2-methylthio-3-methylthiazoline *p*-toluenesulfonate.

Samples for NMR Measurements. Samples were prepared as previously described.[1] The ^{13}C samples were made with, typically, 1.0 mmol of silver nitrate added to every 1 mL of dimethyl-d_6 sulfoxide. The ^{13}C NMR samples of *n*-propylamine containing a ligand-to-silver ratio of more than 3:1 precipitated slightly and were diluted with additional Me_2SO. The dilution, which increased the volume by ~40%, is expected to have a minor effect on observed shifts. For ^{13}C measurements, the concentration of silver nitrate was normally held constant in each experiment, while the ligand concentration was varied. Separate samples were made for each Ag(I):ligand mole ratio used, and the solids were dissolved rapidly with an ultrasonic bath. Amounts of solid ligands were measured by weight, whereas for liquid ligands the density was used to calculate the appropriate volumes, which were then measured with Eppendorff pipets. The concentrations of the ligands in the samples used for ^{13}C analysis without silver nitrate were 2-4 M.

All samples (except ethylenethiourea) used for ^{109}Ag measurements were 1.0 M in $AgNO_3$. Because of solubility limitations, the samples of ethylenethiourea were 0.4 M. For the ^{109}Ag experiments, the mole ratio of Ag(I):ligand was varied by holding the initial $AgNO_3$ concentration constant and varying the ligand concentration.

Some samples were unstable. The silver complex of **2**, particularly, tended to turn dark and form a precipitate. Instability of the silver complex of **10** prevented reproducible measurement of ^{13}C NMR spectra. The instability of the silver complex of thiourea in dimethyl-d_6 sulfoxide has been noted.[10] We found that the complexes of dipropylamine, over time, formed a precipitate and a silver mirror.

Instrumentation. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer with 10-mm tubes at 27 °C. Generally, 200-2000 transients of 1 s were accumulated after excitation pulses corresponding to "flip angles" of 40-60°. Spectral widths were 4000 Hz, with 4K real data points in the transformed spectra. Peak assignments were made with the help of off-resonance, single-frequency decoupling and by comparison of the spectra with those of known compounds in the literature. Chemical shifts were determined relative to the internal deuterium signal of the solvent, which was previously shown to be insensitive to the silver complex concentration.[1] The internal deuterium solvent shift was referenced to tetramethylsilane with calibrations determined from samples containing Me_4Si in the dimethyl-d_6 sulfoxide. Me_4Si itself is only slightly soluble in many of the solutions used. In most cases, the spectra could be reproduced on different samples at the same concentrations to within 0.05 ppm. However, when the ligand was a liquid, the error was somewhat larger, owing to the errors in the volumetric measurement of the sample. The scatter in results for *n*-propylamine might also be related to its decomposition rate, although for the other compounds slight amounts of decomposition did not change the measured chemical shifts.

The ^{109}Ag NMR measurements on all samples except **1** and **2** were made on a highly modified Bruker HFX-90 spectrometer[13] operating at a frequency of 4.19 MHz, interfaced to a Nicolet 1180B data system. The natural-abundance samples were examined in 10-mm tubes at ambient temperature, ca. 33 °C. An external field frequency ^{19}F lock (C_4F_8) was used. The ^{109}Ag measurements made on the Bruker HFX-90 spectrometer were referenced to the ^{1}H solvent resonances to correct for changes in bulk susceptibility.

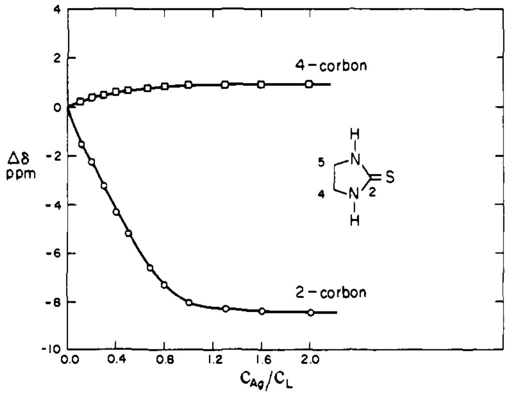

Figure 1. Changes in the ^{13}C chemical shifts of ethylenethiourea (**1**) induced by silver complexation in Me_2SO. The value of $\Delta\delta$ for uncomplexed ligand is zero.

Because of time constraints due to solubility and decomposition problems, ^{109}Ag NMR sensitivity was a problem for some samples. Hence, ^{109}Ag measurements on **1** and **2** were made on a Bruker WH-270 spectrometer at 12.6 MHz, using 15-mm sample tubes. The sample temperature was about 30 °C.

All chemical shifts for both ^{13}C and ^{109}Ag are defined as $\delta_i = (\nu_i - \nu_{\text{ref}})/\nu_{\text{ref}}$, where ν_i is the resonance frequency of the *i*th spin and ν_{ref} is the reference frequency. Shifts defined in this manner are more positive for lower shielding. A 1.0 M $AgNO_3$-Me_2SO solution is taken as the zero chemical shift reference (0.0 ppm) for all ^{109}Ag measurements.

Crude measurements of the pH changes on the formation of the silver complex of **2** were made with a Sargent dual reference and glass pH electrode. As there was some drift during the measurements, the data are considered only qualitative.

Results

In our previous report[1] we showed that, in ideal cases where a series of well-separated equilibria involving different silver complexes is involved, the changes in the ^{13}C chemical shifts of the ligand are particularly informative when plotted vs. the ratio of the analytical concentration of silver, C_{Ag}, and the concentration of the organic ligand, C_L. To the extent that the assumptions hold, such a plot consists of straight-line segments. The connecting points between the straight lines indicate the stoichiometries of the various complexes formed. The changes in the shifts of the silver ion may be analyzed similarly, but the plot of straight-line segments should be obtained when the shifts are recorded vs. the ratio of C_L to C_{Ag}.

Ethylenethiourea (1). This compound was examined because of its similarity to thiourea and tetramethylthiourea. We have reported interesting differences in the NMR results for the latter two compounds.[1]

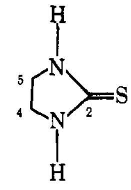

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Figure 1 shows the effect of changing the C_{Ag}/C_L ratio on the ^{13}C chemical shifts of **1**. The greatest shifts produced were for the thiocarbonyl carbon, with a total shift of almost 9 ppm.

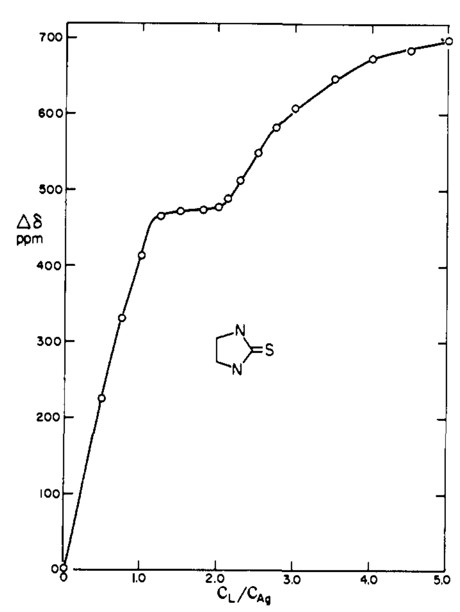


Figure 2. Changes in the ^{109}Ag chemical shift of 0.4 M $AgNO_3$ solutions in Me_2SO induced by complexation with ethylenethiourea (**1**). The value of $\Delta\delta$ for a 1.0 M $AgNO_3$ solution in Me_2SO with no other ligand is zero.

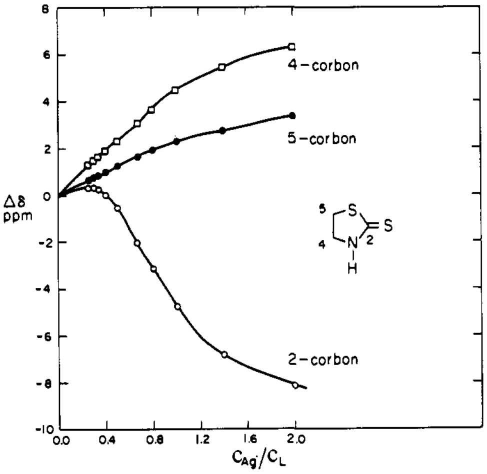


Figure 3. Changes in the ^{13}C chemical shifts in thiazolidine-2-thione (**2**) induced by silver complexation in 1.0 M solutions of $AgNO_3$ in Me_2SO. The value $\Delta\delta$ for uncomplexed ligand is zero.

This value is similar to the total shift found for silver complexes of thiourea. There was a slight leveling off of the curve above C_{Ag}/C_L ratios of 1.0. For thiourea and tetramethylthiourea, there was a slight inflection in the chemical-shift plot around 0.3.[1] This inflection, if it exists at all for ethylenethiourea, was not clearly shown by the data.

The variation of the ^{109}Ag chemical shift upon complexation with **1** is shown in Figure 2. Relative to the uncomplexed Ag(I) cation in Me_2SO, a total shift of about 700 ppm is observed, corresponding to lower shielding. Two distinct break points appear in the curve at C_L/C_{Ag} ratios of 1.1 and 2.0. These two break points do not appear to be reflected significantly in the ^{13}C chemical shifts (Figure 1), which show only a gentle monotonic curve.

Thiazolidine-2-thione (2). The ^{13}C NMR results for this compound are shown in Figure 3. Once again the largest changes in shift occurred for the thiocarbonyl carbon, but the direction of change indicated an initial decrease in shielding of the carbon, with a reversal around C_{Ag}/C_L of 0.3. There was a very gradual leveling off of the curve at higher C_{Ag}/C_L values. The total shift range for the thiocarbonyl carbon of more than 8 ppm is comparable to those found for the thiourea derivatives.[1]

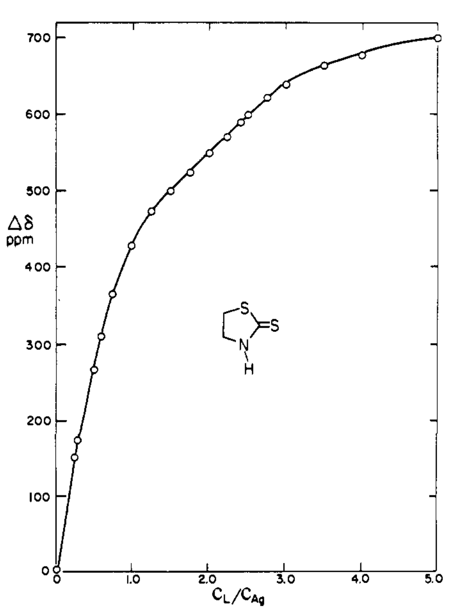
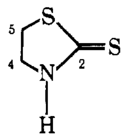


Figure 4. Changes in the ^{109}Ag chemical shift of 1.0 M $AgNO_3$ solutions in Me_2SO induced complexation with thiazolidine-2-thione (**2**). The value of $\Delta\delta$ for a 1.0 M $AgNO_3$ solution in Me_2SO with no other ligand is zero.



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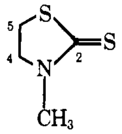
Thiazolidine-2-thione and related compounds are known to complex silver with simultaneous loss of the nitrogen proton.[14] This proton loss was followed crudely in the present work by monitoring of the increase of potential across a glass pH electrode as the ratio of silver to ligand was increased. The apparent pH rose smoothly up to a C_{Ag}/C_L value of 0.5, then flattened out.

The complexation to **2** produced a large but very smooth change in the ^{109}Ag chemical shift (Figure 4). After the usual rapid increase in ^{109}Ag chemical shift as initial amounts of **2** were added, the curve gradually leveled off. The slight inflection in the curve between C_L/C_{Ag} ratios of 2.0 and 2.5 corresponds with the above-mentioned change in direction of the ^{13}C curve (Figure 3, carbon 2).

3-Methylthiazolidine-2-thione (3). Figure 5 shows clearly that the ^{13}C chemical shift changes were much smaller for the methyl-blocked species, **3**, than for the unblocked species, **2**.



3

Furthermore, the largest shifts were no longer for the thiocarbonyl carbon, but for the 4 carbon. The change in the direction of the shifts for the thiocarbonyl carbon again appeared, and again there were no sharp breaks in the curves.

The plot of silver chemical-shift changes with the ratio of C_L to C_{Ag} is shown in Figure 6. The curve is one of the smoothest we have observed for silver complexes, there being no suggestion of breaks or unusual changes in slope.

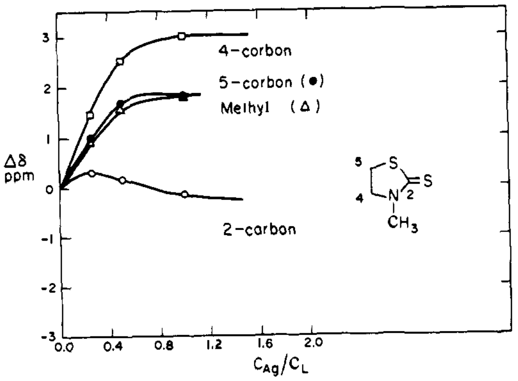


Figure 5. Changes in the ^{13}C chemical shifts in 3-methylthiazolidine-2-thione (**3**) induced by silver complexation in 1.0 M solutions of $AgNO_3$ in Me_2SO. The value of $\Delta\delta$ for uncomplexed ligand is zero.

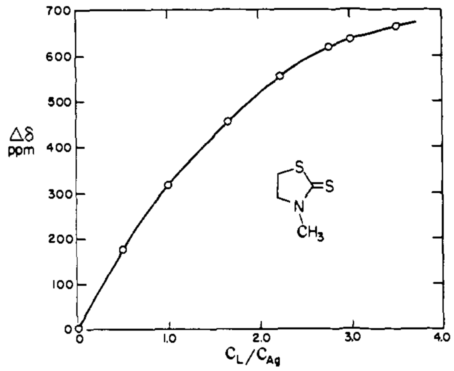
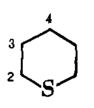


Figure 6. Changes in the ^{109}Ag chemical shift of 1.0 M $AgNO_3$ solutions in Me_2SO induced by complexation with 3-methylthiazolidine-2-thione (**3**). The value of $\Delta\delta$ for a 1.0 M $AgNO_3$ solution in Me_2SO with no other ligand is zero.

Dipropylamine (4). Because of the possible role of unsaturation affecting the results for the above compounds, we chose to examine some simple saturated silver ligands containing sulfur and nitrogen. The results for dipropylamine appear in Figure 7. The largest changes in ^{13}C chemical shifts caused by silver complexation occurred for the carbon attached to nitrogen and indicated that complexation decreased the shielding of that carbon. The sharp break in the curve at a C_{Ag}/C_L ratio of 0.5 is particularly interesting, especially since the chemical shifts became essentially constant for higher values of the silver-to-ligand ratio.

The ^{109}Ag results for dipropylamine are given in Figure 8. There is a rather sharp peak around a C_L/C_{Ag} value of 2 corresponding to the 2:1 ligand-to-silver complex. The silver chemical shift curve does not become entirely horizontal at higher values of C_{Ag}/C_L but continues to rise gradually. Extrapolation of the two straight-line segments puts the break close to but not exactly at a C_{Ag}/C_L value of 2:1.

Pentamethylene Sulfide (5). This compound served as an example of a simple saturated sulfur ligand. As was observed



5

for other ligands bonding silver through sulfur, no sharp breaks were observed in the chemical shift plots (Figure 9). However, the direction of change for the carbon attached to sulfur indicated that its shielding was decreased by complexation, whereas for the thiocarbonyl compounds the carbon attached to sulfur primarily experienced increases in shielding.

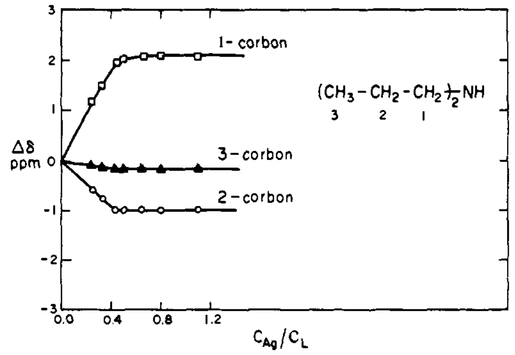


Figure 7. Changes in the ^{13}C chemical shifts in dipropylamine (**4**) induced by silver complexation in 1.0 M solutions of $AgNO_3$ in Me_2SO. The value of $\Delta\delta$ for uncomplexed ligand is zero.

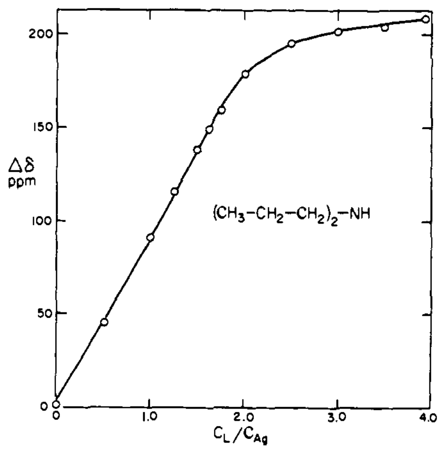


Figure 8. Changes in the ^{109}Ag chemical shift of 1.0 M $AgNO_3$ solutions in Me_2SO induced by complexation with dipropylamine (**4**). The value of $\Delta\delta$ for a 1.0 M $AgNO_3$ solution in Me_2SO with no other ligand is zero.

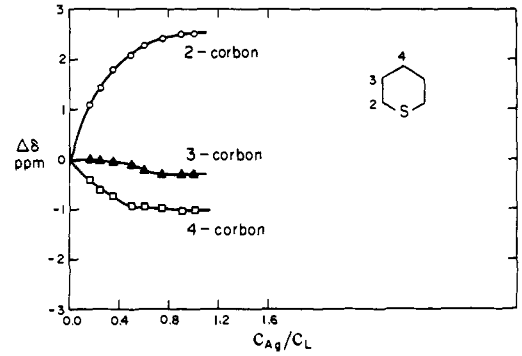


Figure 9. Changes in the ^{13}C chemical shifts in pentamethylene sulfide (**5**) induced by silver complexation in 1.0 M solutions of $AgNO_3$ in Me_2SO. The value of $\Delta\delta$ for uncomplexed ligand is zero.

A plot of the ^{109}Ag chemical shift as a function of the C_L/C_{Ag} ratio for **5** is shown in Figure 10. A very smooth curve is observed, which is almost horizontal at the maximum values of the C_L/C_{Ag} ratio.

2-Aminothiazole (6). This compound was studied because, at least in the tautomeric form, **6a**, it is analogous to the thiazolidine-2-thione, **2**, described above. There is an additional ring double bond in **6**, and we found that the silver complex of the corresponding saturated compound was highly unstable.

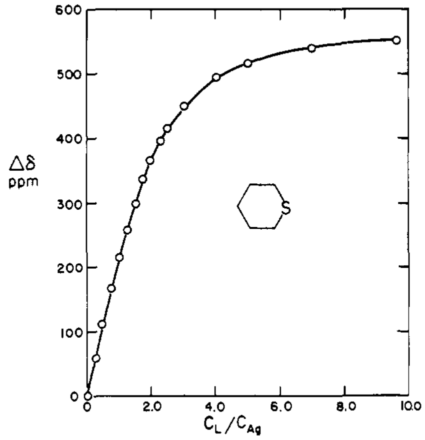


Figure 10. Changes in the ^{109}Ag chemical shift of 1.0 M $AgNO_3$ solutions in Me_2SO induced by pentamethylene sulfide (**5**). The value of $\Delta\delta$ for a 1.0 M $AgNO_3$ solution in Me_2SO with no other ligand is zero.

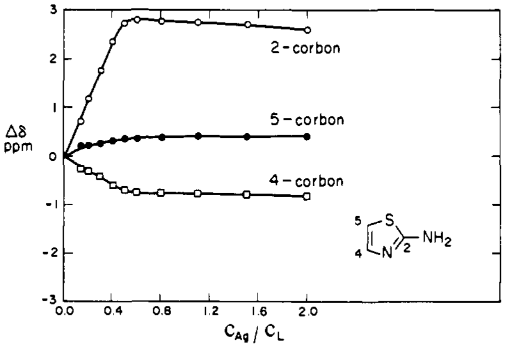
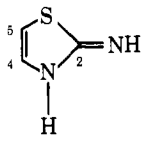
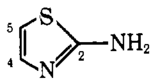


Figure 11. Changes in the chemical shifts of 2-aminothiazoline (**6**) induced by silver complexation in 1.0 M solutions of $AgNO_3$ in Me_2SO. The value of $\Delta\delta$ for uncomplexed ligand is zero.

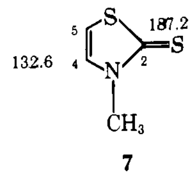


6a

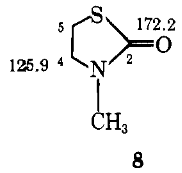


6b

A relevant question for this compound is which is the predominant tautomer, **6a** or **6b**, in the absence of a complexing metal ion. Comparison of ^{13}C chemical shifts of **6** with those of the related compounds **7**, **8**, and **9**, shown below with relevant ^{13}C shift values from the literature,[15-17] does not conclusively support either tautomer for **6**. The chemical shift of C-4 in **6** is 138.4 ppm, intermediate between the values for C-4 in structures with an exocyclic double bond at the β,γ position (132.6 and 125.9 ppm for C-4 in **7** and **8**, respectively) and a structure with an endocyclic double bond at the β,γ position (142.8 ppm for C-4 in **9**).



7



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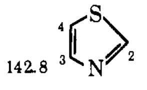


9

Complexation of **6** with silver caused a decrease in the shielding of the 2 carbon with a maximum shift occurring at a C_{Ag}/C_L ratio of about 0.4, followed by a very slight decrease in shielding (Figure 11). There was a sharp break in the chemical shift plot for the 4 carbon at a silver-to-ligand ratio of 0.5, but the plot for the 5 carbon was rather featureless.

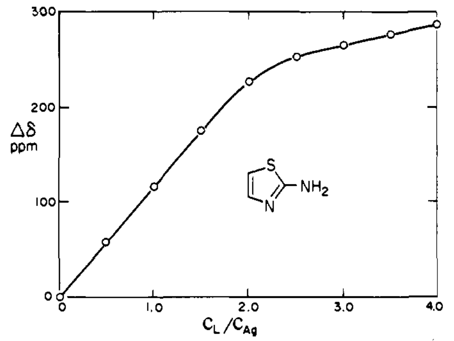
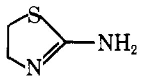


Figure 12. Changes in the ^{109}Ag chemical shift of 1.0 M $AgNO_3$ solutions in Me_2SO induced by complexation with 2-aminothiazoline (**6**). The value of $\Delta\delta$ for a 1.0 M $AgNO_3$ solution in Me_2SO with no other ligand is zero.

Attempts were made to take ^{13}C spectra for **10**, which lacks the additional ring double bond, but the instability of the silver complex prevented precise work. Qualitatively, however, the results were similar to those for **6**, except that the maximum shift range observed for **10** appears to be greater than that for **6**.



10

The ^{109}Ag silver spectra for complexes of **6** were particularly interesting because the resonances had widths of ~6 Hz. We have not observed such broadenings previously for other silver complexes, although we have failed in attempts to obtain spectra of silver complexed with triphenylphosphine, possibly owing to very severe line broadening. As chemical exchange phenomena are one possible cause for this effect, we plan future variable-temperature studies on this system.

A plot of the silver chemical shift changes for **6** is shown in Figure 12. The main feature of the curve is the break around a ratio of C_L to C_{Ag} of 2.0, in agreement with the break in the ^{13}C chemical shift plot at a ratio of C_{Ag} to C_L of 0.5.

Discussion

Appearance of the Chemical-Shift Plots. A basis for analysis of the chemical-shift data was described above and in the earlier report.[1] From the assumption that the formation constants of the various complexes are such that only adjacent species in the series need be considered in any single solution, it was shown that a plot of ^{13}C chemical shifts vs. C_{Ag}/C_L should consist of a series of straight-line segments. The connecting points of the straight lines (or breaks) define the stoichiometries of the complexes in the series. For the ^{109}Ag spectra, the plot of straight-line segments should result from a plot of chemical shifts vs. C_L/C_{Ag}.

The above analysis was not adequate for thiourea or tetramethylthiourea,[1] in that, although there were interesting shapes in the plots, no straight-line (or even approximately linear) segments could be discerned. The results were explained in terms of a breakdown in the basic assumptions, in that there were apparently a number of complexes of only slightly different stability in any given solution. These complex species were thought to include aggregated or polymeric species. Such an explanation could not strictly be proven but was consistent with the observed facts.

Although a complete mathematical simulation of the individual curve shapes in the chemical-shift plots would be interesting when the simple assumptions break down, we have not considered such an analysis justified. In many of the systems the large number of species apparently present would require that an unwieldy number of chemical shifts and equilibrium constants be used in the analysis. Uncertainties in the exact nature and of the chemical shifts of the individual species would further complicate the analysis.

The present data seem to confirm the complexity of solutions in which silver is preferentially bound to an organic ligand through a sulfur atom[14,18] (ligands **1–4**). Although there are rather interesting fluctuations in both the ^{13}C and ^{109}Ag spectra for the sulfur ligands (**1–3** and **5**), these fluctuations are not easily amenable to analysis, particularly when both ^{13}C and ^{109}Ag spectra are considered. Ultimately, when more reference information is available for comparison, it may be possible to determine the various types of species present in the solutions.

By contrast, the ^{13}C chemical shift plot for dipropylamine does come very close to consisting of straight-line segments. The position of the intersection indicates that the primary complex formed is the 2:1 ligand-to-silver species. Silver is known to form very stable complexes with nitrogen donors, consistent with such a conclusion.[19]

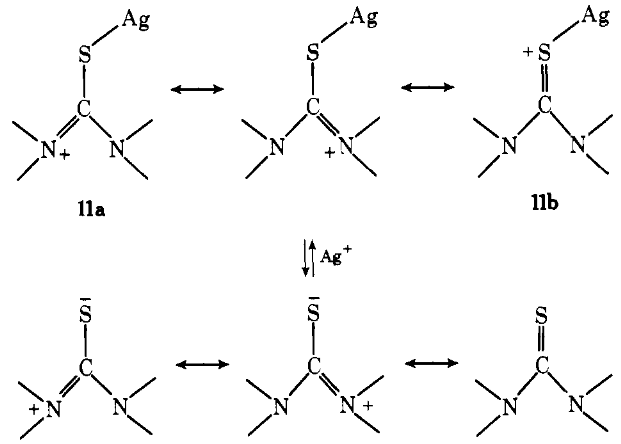
The extrapolated break point in the silver spectrum is not precisely at the point expected for the 2:1 ligand-to-silver complex. Furthermore, for high ligand concentration, the curve does not become completely flat, as would be expected in terms of the formation primarily of a very stable 2:1 ligand-to-silver complex alone. The ^{109}Ag results might indicate some contribution to the observed chemical shift of a small amount of uncomplexed silver ion, or silver in the monoligand complex, even for relatively high ligand concentrations.

The similarity of the ^{13}C and ^{109}Ag data for the aminothiazole **6** and dipropylamine suggests that binding occurs in both compounds through nitrogen and that the 2:1 ligand-to-silver complex is formed most favorably. The behavior of silver toward nitrogen long delayed the recognition that the preferred coordination number with other types of ligands, particularly those of "class B", is often greater than 2.[19a,20,21] Our results are consistent with relatively simple complexing behavior of nitrogen ligands but a more complex situation for sulfur ligands.

Analysis of ^{13}C Chemical Shifts with Silver Complexation. The direction of the shifts in dipropylamine and pentamethylene sulfide can be explained for the carbon next to the heteroatom in terms of simple inductive charge withdrawal on formation of the silver complex. This assumes that the dominant influence on the ^{13}C shift of the α carbon is an electron density effect. Nuclei further away become more shielded with silver complexation, however. Both the 1 and 2 carbons of amines become less shielded on protonation, although the 2 carbon is more strongly affected than is the 1 carbon. Since the protonation results may also be explained in terms of inductive effects, the results for silver complexation should probably be considered cautiously until the general nature of the types of shifts to be expected from the perturbation of an organic molecule by a positive ligand is better understood.

Analysis of the chemical shifts of the unsaturated compounds **1–4** in terms of charge-density effects is clearly not appropriate at the present level of knowledge. For our analysis, it is sufficient to note that thiocarbonyl carbons are generally less shielded than are carbonyl carbons, which are themselves less shielded than are carbons doubly bonded to nitrogen.[22]

Without attempting a fundamental interpretation, we can understand the ^{13}C chemical shifts of the silver complexes qualitatively in terms of the relative contributions of the various resonance structures involving double bonds to the heteroatoms. For example, the effect of silver complexation in thiourea or its derivatives should be to enhance the importance of the resonance form related to **11a** relative to the thione form related to **11b**. Since carbon atoms doubly bonded to nitrogen typically have chemical shifts in the vicinity of 160 ppm, compared to about 220 ppm for carbon doubly bonded to sulfur, silver complexation might be expected to cause an increase in shielding of the S-bonded carbon atom. The possibility that there may be a lower electron density on the thiocarbonyl carbon in the silver complex than in the free ligand is not a controlling factor.



Thiazolidine-2-thione (**2**) and 3-methylthiazolidine-2-thione (**3**) are interesting in terms of the above analysis. The "excess" positive charge in the complex can be distributed by resonance to sulfur as well as to nitrogen in these compounds. Thus, the incremental increase in the importance of C=N bonding might be less than for the thioureas, but the thiocarbonyl carbon should still become more shielded with silver complexation.

The initial change to less shielding of the thiocarbonyl carbons for both **2** and **3** is puzzling, then. That the change of direction of the shifts is not simply due to competing effects caused by the proton ionization and the silver complexation may be deduced from the fact that similar curve shapes are found for **2** and **3**. We have previously surmised that, for low levels of silver relative to ligands such as the thioureas, the predominant mode of silver binding may be different from that at high silver concentrations.[10] Different modes of silver complexation might conceivably be associated with chemical shifts in different directions for the thiazolidinethiones.

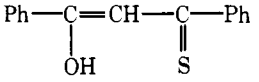
The smaller shifts observed for the methyl-substituted compound **3** than for **2** do not in any sense imply that the strength of the silver binding is less. Rather, the size of the shifts is a direct result of the differences in the electronic structure of the two silver complexes. The silver chemical shifts for **3** cover the full range expected, confirming that it is the ^{13}C chemical shifts that are unusual and not the size of the various equilibrium constants involved.

For 2-aminothiazoline, the shape of the chemical-shift plots alone suggests that binding occurs through nitrogen rather than sulfur, since sharp breaks have not been observed for any sulfur ligands. The fact that the 2-carbon resonance becomes less shielded implies also that the C=S character is greater in the complex than in the free ligand. This is most reasonably explained by complexation at one of the nitrogen atoms rather than at the sulfur. The data do not permit an easy differentiation between the two nitrogens as binding sites, however. One should realize that the possibility exists that the preferred form of **7** (a or b) could change upon complexation with Ag(I). There is even some evidence that **6** complexes silver through complete loss of the proton.[23]

Comparisons with Other Compounds. The direction of the ^{13}C shifts we observe as a result of silver complexation parallels results which have been observed in other systems. The ^{13}C spectra of several thiouronium ions have been reported, and the central carbon is more shielded than is that of the parent compound in spite of the additional positive charge in the derivative.[24] The thiocarbonyl carbons of 6-thioguanosine also become more shielded upon complexation with mercury.[4] The direction of the shifts is analogous to those which we have seen.

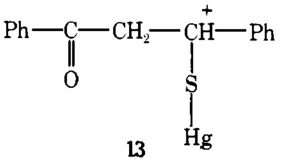
The carbonyl carbons in several amides are more shielded by complexation with various metals.[2b,2d] The shifts are smaller than those found for the thiourea derivatives, consistent with the fact that C=O and C=N carbons absorb at more nearly the same frequency than do C=S and C=N carbons. Amide carbons are apparently deshielded by protonation, however.[9b] Such different behavior for protonation and for metal complexation could be rationalized if protonation occurred on nitrogen rather than oxygen. There has been controversy, but the protonation of amides on oxygen now appears to be most favorable.[25] Thus the different behavior is not at this moment explained. Interestingly, the carbonyl carbons of cationic ethylated urea derivatives are more shielded than are the carbons of corresponding free ligands.[24b] Protonation effects seem to differ from those of complexation by other positive ions.

One pertinent example, the chemical-shift effect of mercury complexation of a thioketone, has been reported.[7] The parent compound **12** probably exists largely as an enol, and the



$\mathrm{Ph{-}\underset{\substack{|\\ OH}}{C}{=}CH{-}\underset{\substack{\|\\ S}}{C}{-}Ph}$

12



$\mathrm{Ph{-}\underset{\substack{\|\\ O}}{C}{-}CH_2{-}\overset{+}{\underset{\substack{|\\ S\\ |\\ Hg}}{CH}}{-}Ph}$

13

chemical shifts suggest that the oxygen rather than the sulfur is involved in the tautomerization. On the other hand, the complex is formed with loss of a proton, and its structure is probably **13**. The olefinic character of the complex would result in a rather large shielding.

Conclusions

The compounds studied show further the utility for the study of silver complexes by both ^{13}C and ^{109}Ag NMR. Additional improvements in technique are needed, however, so that much lower concentrations can be used. As more data and structure/shift relationships are developed, further conclusions about structural detail will be possible.

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