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Complexation of Silver(I) with Thiourea and Tetramethylthiourea in Dimethyl Sulfoxide Solution as Studied by ^{13}C and ^{109}Ag Nuclear Magnetic Resonance Spectroscopy

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Abstract: A combination of ^{13}C and ^{109}Ag NMR spectroscopy has been used to study silver complexes of thiourea and tetramethylthiourea in dimethyl sulfoxide solution. The results are consistent with the presence of a variety of complex species for the concentrations used (approximately 1 M in silver ion with varying ligand concentrations) including highly aggregated forms. The combination of metal ion NMR and ^{13}C NMR appears to have general utility for the study of silver complexes, but instrumental improvements allowing for the study of solutions of lower concentrations are needed.

Increasingly, NMR spectroscopy is expanding beyond the study of "traditional" nuclei such as ^1H and, more recently, ^{13}C to include many other less common and, in many cases, more difficult nuclides.[1] For example, a number of metal nuclides have been examined in recent years with regard to possible information about solvation, ion pairing, and structure of organometallic compounds. Previous reports dealing with the silver nuclides, ^{109}Ag and ^{107}Ag, have been few, however.[2,3]

Metal complexes have also been studied in a variety of cases with ^{13}C NMR.[4] Carbon NMR has the potential of being especially informative about the binding site in an organic ligand, particularly if the interaction occurs through a functional group containing a centrally located carbon atom, such as a carbonyl group. It has already been used to study several silver complexes.[5] In a few cases, spin–spin coupling of the silver nuclei with carbon has been observed.[6] In general, however, the lability of most silver complexes averages such splittings to zero.

It appeared to us that the combined use of ^{13}C and ^{109}Ag NMR spectroscopy would offer a particularly powerful means of studying silver complexes in solution. The greatest problem to such an approach is the low inherent sensitivity of the ^{109}Ag nucleus (spin ½, natural abundance of 49%, NMR sensitivity relative to ^1H of 1.01×10^{-4} per nucleus, and very long relaxation times). Nevertheless, we have observed that ^{109}Ag spectra of usable quality can be obtained from solutions with 1 M Ag(I) concentrations with no more than a few hours of signal averaging;[7] ^{13}C spectra are now obtained easily for such solutions.

Although we hope eventually to be able to study a wide variety of silver complexes in concentrations of 0.1 M or lower, for the present time we have chosen to examine solutions containing 1 M silver nitrate in dimethyl sulfoxide (Me_2SO) with varying concentrations of thiourea and tetramethylthiourea. We made this choice for the following reasons: (1) thiourea and, presumably, tetramethylthiourea form complexes with silver(I) which have a variety of stoichiometries and high thermodynamic stabilities;[8-23] (2) crystal structures of isolated solids have been determined for some of these complexes;[24-25] (3) both thiourea and tetramethylthiourea are soluble up to at least 3 M with 1 M silver nitrate in dimethyl sulfoxide.

Dimethyl sulfoxide itself is believed to interact only weakly with silver(I), apparently through the oxygen atom.[26] Furthermore, since silver(I) is a "class b" metal,[27] one expects it to be only weakly solvated even in water. Solvent effects on the stability of the complexes may thus be relatively small, although presumably not completely negligible.[28] As a result, information about silver complexes obtained from Me_2SO solutions may be directly relevant to the properties of the same complexes in water.

This work was specifically designed to test the ability of NMR spectroscopy to reveal several types of information: (1) A determination of the binding site or sites in the organic ligand is important. (2) Specific information about the type of bonding between the ligand and the metal ion may be available from the NMR data in those cases where the empirical and/or theoretical correlations are far enough advanced for the types of systems of interest. For example, thiourea can act as both a bridging and terminal ligand with silver(I),[24,25] and the particular bonding involved in a given complex may be reflected in the NMR data. (3) The stoichiometries of the various complexes formed may also be found. In some cases, measures of the stability (equilibrium constants) of these complexes may also be possible.

Experimental Section

^{109}Ag spectra were obtained at 4.19 MHz from samples in natural abundance in 10-mm tubes on a modified Bruker HFX-90 NMR spectrometer as was previously described.[7] The shifts reported here were measured relative to the Me_2SO proton resonance. Bulk susceptibility corrections were found to be negligible, as the Me_2SO proton chemical shifts varied by less than ±0.3 ppm.

Solutions for the silver spectra were prepared in volumetric flasks with 1 M concentrations of silver nitrate (Eastman) in dimethyl sulfoxide (Fisher ACS Certified Reagent Grade). Solutions were freshly made before use by completely dissolving the silver nitrate, then dissolving the ligands (both from Eastman). The Me_2SO was used without special drying procedures, since silver chemical shifts are affected negligibly by small amounts of dissolved water.[7]

The tetramethylthiourea solutions showed no appreciable color change over a period of 2 or 3 days, but the thiourea solutions gradually turned dark over a period of hours. A black precipitate was formed, which is probably silver sulfide; the overall reaction is analogous to reactions which occur in water for a variety of silver complexes of thioamides having an ionizable proton.[29] The process occurs especially fast when the concentration of thiourea is low relative to that of silver.

^{13}C spectra were recorded on a Varian CFT-20 spectrometer with either 8- or 10-mm sample tubes. Generally, 200–2000 transients of 1 s were accumulated with pulse angles of 40–60°. Spectral widths were 4000 Hz with 4K real data points in the transformed spectrum. The probe temperature was 27 °C.

Tetramethylsilane (Me_4Si) is only moderately soluble in Me_2SO, and the solubility is reduced by the presence of silver nitrate. Therefore, ^{13}C NMR peak positions were measured indirectly relative to the deuterium lock signal through the transmitter offset of the spectrometer. The position of the lock signal was checked in several samples which did contain Me_4Si, and it was found that the position of the Me_4Si relative to the lock was constant within 0.1 ppm. The carbon resonances of the solvent were found to vary as much as 0.3 ppm in different samples, however. Chemical shifts could be reproduced on different samples on different days within a range of 0.05 ppm.

For convenience the samples for ^{13}C analysis were made with 0.1522 g (0.0025 mol) of silver nitrate (Eastman 491) in 2.5 mL of dimethyl-d_6 sulfoxide (Stohler) as measured from an Eppendorf pipet. The ligand was dissolved completely, then silver nitrate was dissolved with an ultrasonic bath. Samples of ligand without silver nitrate contained 0.008 mol of thiourea and 0.0057 mol of tetramethylthiourea, respectively, in 2.0 mL of dimethyl-d_6 sulfoxide.

Method of Data Analysis. It seemed feasible that ^{13}C chemical shifts would be indicative of the binding sites in the ligand molecules. Binding sites might also be reflected by the ^{109}Ag shifts. Sensitivity of the chemical shifts of other metal nuclides to the nature of binding ligands has been demonstrated.[30] We have attempted to study the complexes of both thiourea and tetramethylthiourea with silver(I) by measuring ^{109}Ag and ^{13}C chemical shifts for a number of solutions having a constant silver ion concentration and varying concentrations of the organic ligand. This procedure gives us potential access to a large range of data not only about binding sites, but also about other aspects of complex structure and stoichiometry.

In general, silver complexes are highly labile. We would expect, therefore, that there would be rapid exchange on the NMR time scale among all silver-containing species in solution. As a result, spin–spin splitting involving the silver nuclei will be averaged to zero. Further, the various corresponding carbons in the different complexes each will give rise to only a single line with a chemical shift representing the weighted average of the chemical shifts of the individual species.

For the purposes of initial analysis, we assumed that a series of mononuclear complexes of high thermodynamic stability is formed. The literature suggests that such an assumption is reasonable.[12,16,18,19,21] We further assumed as a limiting case for discussion that the formation constants of successive complexes are sufficiently separated that only two complexes exist together in appreciable concentration in any given solution.

It is readily shown that under these assumptions the following relations hold for the ^{13}C NMR signals where the two species AgL_n and AgL_{n+1} are the only ones in appreciable concentration.

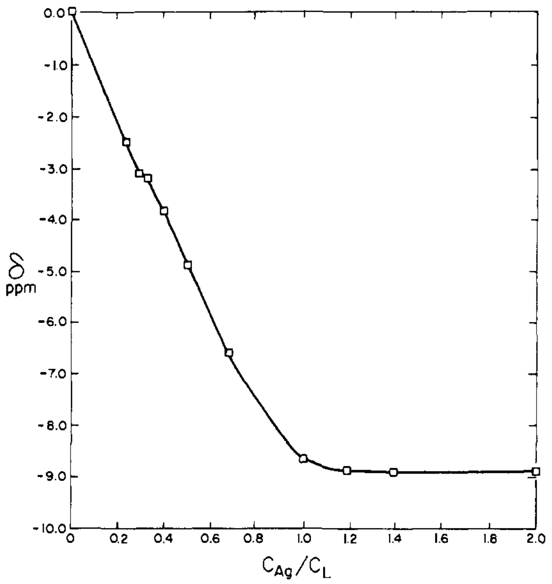


Figure 1. Changes in the ^{13}C chemical shift of the thiocarbonyl carbon of thiourea in Me_2SO induced by silver complexation. Negative values indicate greater shielding. The squares are for clarity only and are much larger than the actual errors in the measurements.

$$\begin{aligned}\nu_{\mathrm{obsd}} &= n\frac{[\mathrm{AgL}_n]}{C_\mathrm{L}}\nu_{\mathrm{AgL}_n} + (n+1)\frac{[\mathrm{AgL}_{n+1}]}{C_\mathrm{L}}\nu_{\mathrm{AgL}_{n+1}} \\ &= n\frac{(n+1)C_{\mathrm{Ag}} - C_\mathrm{L}}{C_\mathrm{L}}\nu_{\mathrm{AgL}_n} + (n+1)\frac{C_\mathrm{L} - nC_{\mathrm{Ag}}}{C_\mathrm{L}}\nu_{\mathrm{AgL}_{n+1}} \\ &= n(n+1)(\nu_{\mathrm{AgL}_n} - \nu_{\mathrm{AgL}_{n+1}})\frac{C_{\mathrm{Ag}}}{C_\mathrm{L}} - n\nu_{\mathrm{AgL}_n} + (n+1)\nu_{\mathrm{AgL}_{n+1}} \qquad (1)\end{aligned}$$

where ν_{obsd} is the observed chemical shift and ν_{AgL_n} and $\nu_{\mathrm{AgL}_{n+1}}$ are the chemical shifts of AgL_n and AgL_{n+1}, respectively. C_L and C_{Ag} represent the analytical concentrations of ligand and Ag(I). On the basis of this development (eq 1), it is seen that a plot of the observed carbon chemical shifts vs. C_{Ag}/C_L should be linear. Then, if we consider the entire range of concentration ratios as constituting simply a superposition of regions for which this kind of analysis holds for two species, one expects that a plot of ν_{obsd} vs. C_{Ag}/C_L should be a series of connecting straight-line segments. The positions of the "breaks" which connect the straight lines are indicative of the stoichiometries of the complexes formed. Of course, this is only a limiting case, and one might expect various degrees of rounding about the "breaks", due to contributions of more than two species in a given region of the plot. Some such cases may be sufficiently severe that the breaks are not distinguishable and the model is not useful. Also, if the values of ν_{AgL_n} and $\nu_{\mathrm{AgL}_{n+1}}$ are very similar for some species, this type of analysis would be difficult to employ, but it does provide a convenient starting point.

Relations analogous to eq 1 can be derived for the silver chemical shifts, but the plot of connected straight lines for the silver shifts should be obtained with a plot of the observed ^{109}Ag line position vs. C_L/C_{Ag}. As a result, for a series of mononuclear complexes with increasingly larger ratios of ligand to silver, the breaks will be evenly spaced in the plot of the silver chemical shifts, but will be compressed toward small values of C_{Ag}/C_L for the carbon shifts.

Results

^{13}C Studies. The plot of the ^{13}C chemical shift of the thiocarbonyl carbon in thiourea vs. C_{Ag}/C_L is shown in Figure 1. The curve appears to be linear or almost linear for values of C_{Ag}/C_L between 0.0 and 0.3, then undergoes a slight inflection between 0.3 and about 0.35. There is a noticeable flattening of the curve around a C_{Ag}/C_L value of 1. Although the inflection around 0.3 is slight, it is entirely reproducible with repeated preparations of the solutions on different days. The feature is also apparent when the entire experiment is repeated with constant thiourea concentration and variable silver nitrate

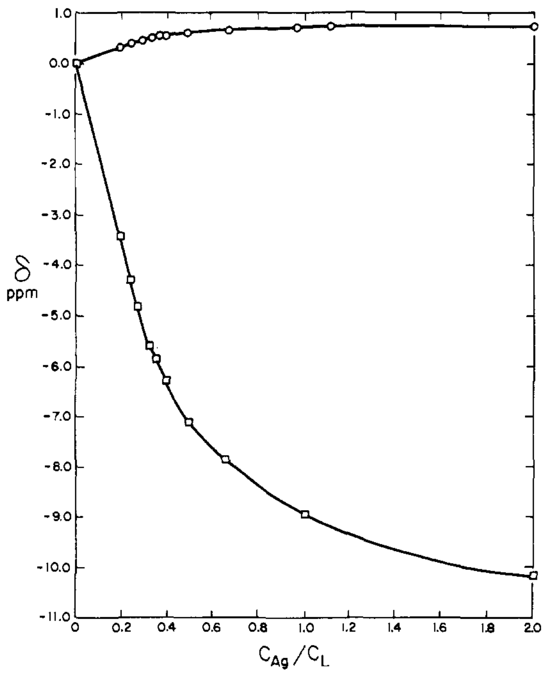


Figure 2. Changes in the ^{13}C chemical shift of the methyl (upper) and thiocarbonyl (lower) carbons of tetramethylthiourea in Me_2SO induced by silver complexation.

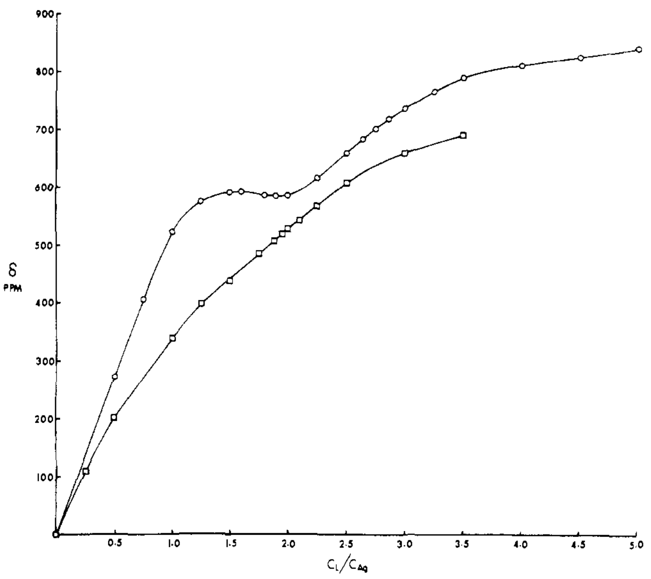


Figure 3. Changes in the ^{109}Ag chemical shift of silver nitrate in Me_2SO induced by complexation with thiourea (circles) and tetramethylthiourea (squares). More positive values of δ indicate decreased shielding.

concentration, and the changes in the curve are well within the experimental error.

The ^{13}C results for tetramethylthiourea are shown in Figure 2. The curve is linear for the thiocarbonyl carbon between 0.0 and about 0.33, and once again, there is a very slight inflection between 0.33 and 0.38. There is a gradual flattening of the plot in the vicinity of C_{Ag}/C_L equal to 1, but the effect is much less pronounced than for thiourea.

The chemical shift of the methyl carbons in tetramethylthiourea is much less affected by silver complexation than that for the carbonyl, and most of the change occurs between 0.0 and 0.5. There are no noticeable inflections for the methyl curve.

^{109}Ag Studies. As is shown in Figure 3, a plot of the observed ^{109}Ag chemical shift vs. C_L/C_{Ag}, a very dramatic reduction of shielding of the silver nucleus is induced by complexation with either thiourea or tetramethylthiourea. When complexed with such sulfur ligands, silver resonances are deshielded by as much as 400 ppm as compared to when the silver is solvated by or complexed with either nitrogen or oxygen ligands; this large reduction in shielding appears to be characteristic of the Ag(I) bonding to sulfur. The total range of silver shifts which have now been observed is over 1000 ppm.[7]

Although the curve for the tetramethylthiourea chemical shifts is monotonically increasing for higher ligand concentrations, the curve for thiourea goes through an interesting S-shape. Careful examination of the plot for tetramethylthiourea, however, shows that there are changes in its slope at C_L/C_{Ag} ratios of about 1.3 and 2.7. There may also be a slight flattening of the curve at higher ligand concentration, but solubility problems prevented a study with concentrations as high as were used for thiourea.

Discussion

Complexes of thiourea and silver ion have been studied by a number of workers,[8-25] and evidence has been presented that in solution various species are formed which have ligand-to-silver ion ratios of 1:1, 2:1, 3:1, 4:1, and 3:2. In some cases solid samples of thiourea complexes with various silver salts have also been obtained. The ligand-to-silver ratios in these solid salts have been either 1:1, 2:1, 3:1, or 3:2.

Crystal structures have been determined for the 3:1 (ligand/Ag(I)) complex of thiourea and silver perchlorate[25] and the 2:1 complex of thiourea and silver chloride.[24] The 3:1 complex is dimeric, with bridging thiourea groups connecting four-coordinate silver ions. The 2:1 complex is polymeric, with an equal number of bridging and terminal thiourea groups. The silver ions are four-coordinate with chloride ions filling the fourth site.

All of the thiourea complexes have high thermodynamic stabilities in aqueous solution relative to the uncomplexed species, the logarithms of the successive formation constants being 5.5–7.0, 10.5–11.0, 12.8–13.5, and about 13.6 (for log β_1, log β_2, log β_3, and log β_4, respectively).[12,16,18,19,21] One report indicates that the logarithm of the formation constant for the 3:2 (ligand/Ag(I)) complex is even larger,[19] about 23. The logarithm of the formation constant of the 3:1 complex has been found[16] for the mixed solvents of water and acetone or water and dioxane to be between 14 and 16. The relatively small effect of solvent on the complex stability is consistent with the fact that silver is a "class b" metal and is not expected to be specifically solvated by oxygen-donor solvents such as water.[31]

By contrast with thiourea itself, complexes of silver(I) with substituted thioureas have received relatively little attention. The stabilities of complexes in solution of monomethylthiourea and dimethylthiourea have been determined,[18b] and there has been a crystal structure determination of the 3:1 (ligand/Ag(I)) complex of monomethylthiourea with silver chloride.[32] Unlike the 3:1 solid complex of thiourea,[25] it is monomeric with three terminal ligand groups. The fourth site around the silver ion is occupied by chloride.

In light of the above-mentioned reports, our own results present at least two puzzles. First, in terms of the type of analysis given above and the fact that thiourea forms a series of very stable complexes with silver(I), it is surprising that there are not more pronounced breaks in the curves in Figures 1 and 2. These breaks should correspond to the various types of complexes which are formed. Second, one might expect that a large shift in the carbon spectrum would occur as the ligands pass from the free state to a bound state. Subsequent changes from one complex to another might have relatively minor effects on the chemical shifts of the ligand if the chemical environment of the ligands were similar from one complex to another. Instead, in Figures 1 and 2, there is an even greater change in the chemical shift between the C_{Ag}/C_L ratios corresponding to the 2:1 and 1:1 complexes (0.5 and 1.0) than there is between the points corresponding to the free ligand and the 4:1 complexes (0.0 and 0.25).

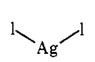
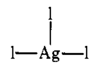
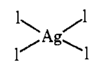
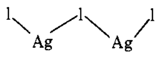
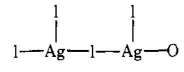
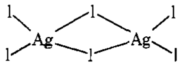
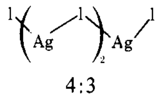
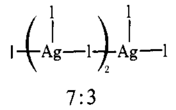
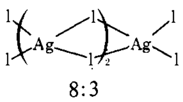
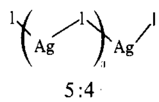
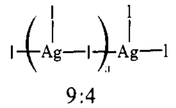
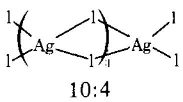
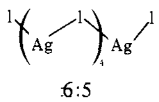
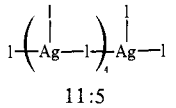
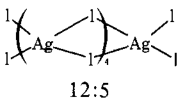
One likely solution to these puzzles is that we have not, so far, taken into account the effect of aggregation of complexes in the interpretation. Possible aggregation of complexes of thiourea in solution has been considered by some authors,[14,19] but generally has been ignored. Nevertheless, the crystal structure of the 2:1 (ligand/silver) complex is clearly polymeric,[24] and the solid 3:1 complex of thiourea with silver nitrate is dimeric.[25] The presence of large numbers of aggregates would make unlikely our initial assumption that the various species are all widely separated in stability.

Ag(I) is known to form complexes with coordination numbers of two, three, and four. The higher numbers are favored by "class b" ligands, such as those which bond through sulfur.[33] In each of the isolated complexes of Ag(I) and thiourea, for example, the coordination number was four, although in some cases, the fourth site was filled by the counterion. For the purposes of data analysis, therefore, we can envision three different series of polymeric aggregates of thiourea silver ion complexes; these are summarized in Table I. In the first series, silver is always bonded to two thiourea groups, in the second, to three, and in the third, to four. The stoichiometry of each complex (ligand/Ag(I) and Ag(I)/ligand ratios) is given underneath its formula in Table I. Of course, in reality, mixed polymers could also occur, and additional silver sites could be filled by the counterion or solvent.

Each of the complexes previously reported in the literature falls naturally into one of the three series in Table I, including the interesting 3:2 (ligand/Ag(I)) complex. A 2:1 complex occurs in all three series, but with different structures. The structure of the solid complex actually isolated and characterized corresponds to what is shown for the three-coordinate series. The 3:1 complex occurs in the monomeric form in the three-coordinate series, but as a dimer in the four-coordinate series. The 3:1 complex of thiourea and silver nitrate actually is dimeric in the solid, but the complex of monomethylthiourea and silver chloride is monomeric.

The stoichiometries of the three-coordinate series and the four-coordinate series overlap, but those of the two-coordinate series are clearly separated, with the border line being the 2:1 complex. One might expect that the stabilities of many of these different forms (at least for a particular coordination type) would not be widely separated. As a result, in any given solution there might be substantial concentrations of a variety of them. Those species in the two-coordinate series would, however, be favored by relatively low concentrations of ligand, while those in the other two series would be favored by high concentrations of ligand. Taking into account various "mixed" polymeric species does not substantially change the picture, but does add new complexes with stoichiometries between about 1.3:1 and 2:1 for polymeric chains containing less than five silver ions. Overall, one would predict that there will be a gradual change from a predominance of complexes in which silver is coordinated to three or four thioureas to a predominance of species in which silver is coordinated to two thioureas as C_L/C_{Ag} changes from 2 to 1. It is precisely in this region that the unusual S-shaped portion of the curve for thiourea occurs in Figure 3. For the tetramethylthiourea curve, there also appears to be a change in the slope of the curve in this area which may be indicative of an analogous but less pronounced change in the overall ligand environment of the silver ions in this case. The dramatic differences between these two curves in this C_L/C_{Ag} region may indicate that the presence of the methyl groups in tetramethylthiourea prevents some specific structural situation to arise in a Ag(I) complex with this ligand, a feature associated with the S-shaped portion of the thiourea curve.

Table I. Polymeric Thiourea–Silver Complexes[a] Considered

2-Coordinate[b] silver	3-Coordinate[b] silver	4-Coordinate silver
 2:1 2.00 0.50	 3:1 3.0 0.33	 4:1 4.0 0.25
 3:2 1.50 0.67	 5:2 2.5 0.40	 3:1 3.0 0.33
 4:3 1.30 0.75	 7:3 2.33 0.43	 8:3 2.67 0.38
 5:4 1.25 0.80	 9:4 2.25 0.44	 10:4 2.50 0.40
 6:5 1.20 0.83	 11:5 2.20 0.45	 12:5 2.40 0.42
1:1 1.0 1.0	2:1 2.00 0.50	2:1 2.0 0.50

[a] Stoichiometric ratio of ligand-to-silver(I) given underneath with the corresponding numerical ratio of ligand-to-silver (left) and silver-to-ligand (right) following. [b] Additional sites could be filled by solvent or the counterion.

With regard to the C_{Ag}/C_L ratio (which is the relevant parameter for discussion of the ^{13}C spectra), the only substantial gap in the array of possible species included in Table I occurs between 0.0 and 0.25. This is the region in which the curves for both thiourea and tetramethylthiourea are approximately linear. There is close spacing of the various Ag(I)/ligand ratios included in Table I throughout most of the rest of the range of ratios, especially since various mixed complexes may contribute additional values between about 0.5 and 0.8. A multiplicity of species present for these C_{Ag}/C_L ratios would account for the absence of pronounced breaks in the curves of Figures 1 and 2 for these ranges, since our analysis assumed only two species present at any one time.

Table I further suggests that more thiourea molecules become located in bridging sites as the silver ion-to-ligand ratio increases. Such a trend would account for the smooth change in the chemical shift over most of the range of C_{Ag}/C_L values. The slight bend in the curves of Figures 1 and 2 at around 0.33 (C_{Ag}/C_L) suggests that the chemical shift of the ligands in the 3:1 (ligand/Ag(I)) complexes are not terribly different from those in the 4:1 complexes. Especially if the 3:1 complex is mostly monomeric, the ligands would be mostly terminal for both of these complexes.

The polymeric nature of various of the complexes of thiourea with silver ion, including the 3:2 (ligand/Ag(I)) species has been inferred previously from solubilities.[14] In addition, cryoscopic measurements have been made with solutions of 0.1 M silver perchlorate and thiourea which show extensive polymerization for the complexes having the empirical formulas 1:1, 3:2, and 2:1. The 3:1 complex appears to be capable of forming only dimers.[19] These results are completely consistent with our interpretation that aggregation does occur and plays an important role in influencing our observed NMR results.

Finally, we point out that the thiocarbonyl carbon becomes more shielded upon complexation to the silver ion. The direction of this shift may be indicative of extensive rehybridization around the atoms involved in the double bond. Similar shifts have been noted for the conversion of thioureas into thiouronium salts[34] and for complexation of thiolated nucleotides with mercury(II).[35]

Conclusions

The multinuclear NMR approach is found to have general utility for the study of silver complexes in solution. Although neither ^{13}C NMR nor ^{109}Ag is capable of providing definitive results for the thiourea complexes of silver, a combination of the two suggests a scenario that is consistent with Ag(I) bonding at sulfur and with other known facts in this area. This scenario includes as an important feature the concept of aggregation, a concept especially applicable to this study, in which high solute concentrations were employed. It seems likely that aggregate species should probably also be considered in studies of complexation of thiocarbonyl compounds with silver ions and other metals at lower concentrations. The presence of aggregates might, for example, explain why drastically different values of entropies and enthalpies of formation of silver complexes of thiourea have been reported previously. Comparisons with data obtained at lower solute concentrations would be useful for studying aggregation. In order for the NMR approach for studies of Ag(I) chemistry in solution to be extended, improvements in experimental sensitivity are clearly needed to permit work at lower concentrations. The use of much larger sample tubes, higher magnetic fields, and refocusing techniques should be beneficial. We are currently exploring such methods and are examining the spectra of additional silver complexes.

Acknowledgment. G. E. Maciel and J. J. H. Ackerman gratefully acknowledge grants from the Eastman Kodak Company and the National Science Foundation (No. MPS74-23980), which partially supported this research, and grants from the National Science Foundation for purchase of equipment used in the ^{109}Ag NMR measurements.

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