

Multinuclear NMR (^1H , ^{13}C , ^{15}N and ^{107}Ag) studies of the silver cyanide complexes of thiourea and substituted thioureas

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Abstract

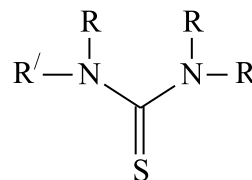
The NMR (^1H , ^{13}C , ^{15}N and ^{107}Ag) studies of the silver(I) cyanide (AgCN) complexes of thiourea (Tu), *N,N'*-dimethylthiourea (Dmtu) and tetramethylthiourea (Tmtu) were carried out in dimethyl sulfoxide. An upfield shift in ^{13}C NMR and downfield shifts in ^1H , ^{15}N and ^{107}Ag NMR are consistent with the sulfur coordination to silver(I). The NMR data shows that >C=S-AgCN complexes are stable in solution and do not undergo disproportionation reactions.

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Keywords: Silver(I) complexes; Silver cyanide; thioureas; NMR

1. Introduction

Recently, it has been established that thiourea and substituted thioureas form stable complexes with AgCN and the crystal structures of the complexes were also determined [1]. However, the solution studies of these complexes were not carried out. Therefore, in the present study we carried out the NMR investigation for three of these complexes [TuAgCN, DmtuAgCN (existing as $\{\text{Ag}(\text{Dmtu})_2\text{Ag}(\text{CN})_2\}$) and [TmtuAgCN] with the aim to study their disproportionation reactions in solution, as observed for the analogous AuCN complexes. For LAuCN-type complexes, it was observed that they underwent disproportionation in solution forming $[\text{AuL}_2]^+$ and $[\text{Au}(\text{CN})_2]^-$ species [2–8]. These reactions are favored by the very large formation constant of $[\text{Au}(\text{CN})_2]^-$ ($\log \beta = 36$) [9]. In the present study we were unable to observe such disproportionation for the AgCN complexes, most probably because the formation constant of $[\text{Ag}(\text{CN})_2]^-$ ($\log \beta = 20$) [10] is significantly lower than that of $[\text{Au}(\text{CN})_2]^-$. However, the study provides useful NMR data for the AgCN complexes. The structures of the ligands are shown as below



where,

R, R' = H for Tu,
R, = H; R' = CH₃ for Dmtu,
R, R' = CH₃ for Tmtu.

2. Experimental

2.1. Preparation of the complexes

Silver cyanide (AgCN) was prepared by mixing the aqueous solutions of AgNO₃ and KCN (unlabeled and ^{13}C , ^{15}N labeled), keeping KCN as a limiting reactant [10]. Mixing immediately resulted in the formation of white precipitates, which were washed with acetone and ether.

The complexes were prepared according to the published procedure [1] (except that they were prepared in a water–methanol mixture) by mixing the solutions of thioureas and AgCN (10% ^{13}C and ^{15}N labeled) in methanol and water, respectively, in the molar ratios of 1.2:1 and

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