

## Silver cyanide complexes of heterocyclic thiones

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### Abstract

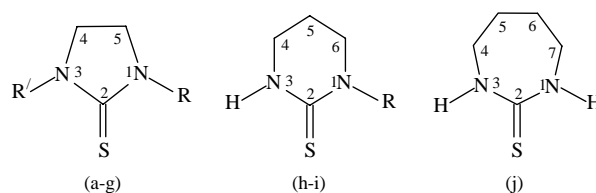
Silver(I) cyanide complexes of various thiones (imidazolidine-2-thione, diazinane-2-thione and their derivatives) have been prepared and characterized by elemental analysis, i.r. and n.m.r. ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{107}\text{Ag}$ ) spectroscopy. It appears from the i.r. data that six out of the ten complexes are nonionic  $[>\text{C}=\text{S}-\text{Ag}-\text{CN}]$  while the remaining four exist as ionic species  $[\text{Ag}(>\text{C}=\text{S})_2]^+[\text{Ag}(\text{CN})_2]^-$  in the solid state. An upfield shift in the  $^{13}\text{C}$ -n.m.r. and downfield shifts in the  $^1\text{H}$ -,  $^{15}\text{N}$ - and  $^{107}\text{Ag}$ -n.m.r. spectra are consistent with the sulfur coordination to silver(I). The n.m.r. data shows that the  $[>\text{C}=\text{S}-\text{Ag}-\text{CN}]$  complexes are stable in solution and do not undergo redistribution.

### Introduction

Complexes of heterocyclic thiones such as imidazolidine-2-thione (Imt), diazinane-2-thione (Diaz) and their derivatives with transition metals are of interest in bioinorganic chemistry because of the search for simple model compounds for metal proteins [1, 2]. In view of this, copper(I) [3], silver(I) [4, 5], gold(I) [6–8], mercury(II) [9, 10] and cadmium(II) [11] complexes with thiones have been widely studied in recent years. We have been investigating the coordination chemistry of  $>\text{C}=\text{S}$  ligands with  $d^{10}$  metal ions in an attempt to assess their mode of binding and to study their physical properties [4, 6–8, 12, 13]. As an extension of our interest in the structural chemistry of metal–sulfur interactions, the work on silver cyanide complexes of thiones has been initiated [14]. In our previous work we reported the n.m.r. studies of three  $[\text{LAgCN}]$  complexes ( $\text{L}$  = thiourea and a substituted thiourea), with the aim of studying their disproportionation in solution, as observed for the analogous  $\text{AuCN}$  complexes [18]. The present report describes the synthesis of silver cyanide complexes of a series of heterocyclic thiones and their characterization by i.r.,  $^{13}\text{C}$ -,  $^{15}\text{N}$ - and  $^{107}\text{Ag}$ -n.m.r. spectroscopy. The structures of thiones used in this study are depicted in Scheme 1.

Stocker *et al.* reported the X-ray structures for several  $\text{L}-\text{Ag}-\text{CN}$  complexes, where  $\text{L}$  = thiourea and substituted thioureas [15]. The X-ray studies showed that some of the complexes exist as mononuclear species,  $\text{L}-\text{Ag}-\text{CN}$ , while the other exist in the ionic form,  $[\text{Ag}(\text{CN})_2\text{Ag}(\text{L})_2]$  in the solid state. However, spectroscopic (i.r. or n.m.r.) measurements for these complexes were not carried out. In this study an attempt has been made to correlate the structural properties with the spectroscopic data for various types of silver(I) com-

plexes:  $[>\text{C}=\text{S}-\text{Ag}-\text{CN}]$ ,  $[>\text{C}=\text{S}-\text{Ag}-\text{NO}_3]$  and  $[\text{Ag}(>\text{C}=\text{S})_2]\text{NO}_3$ .



- (a)  $\text{R} = \text{R}' = \text{H}$ ; imidazolidine-2-thione (Imt)
- (b)  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ; *N*-methylimidazolidine-2-thione (MeImt)
- (c)  $\text{R} = \text{Et}$ ,  $\text{R}' = \text{H}$ ; *N*-ethylimidazolidine-2-thione (EtImt)
- (d)  $\text{R} = n\text{-Pr}$ ,  $\text{R}' = \text{H}$ ; *N*-propylimidazolidine-2-thione (PrImt)
- (e)  $\text{R} = i\text{-Pr}$ ,  $\text{R}' = \text{H}$ ; *N*-(*i*-propyl)imidazolidine-2-thione (*i*-PrImt)
- (f)  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Me}$ ; *N,N*-dimethylimidazolidine-2-thione ( $\text{Me}_2\text{Imt}$ )
- (g)  $\text{R} = \text{Et}$ ,  $\text{R}' = \text{Me}$ ; *N*-ethyl-*N*-methylimidazolidine-2-thione (EtMeImt)
- (h)  $\text{R} = \text{H}$ ; 1,3-diazinane-2-thione (Diaz)
- (i)  $\text{R} = \text{Et}$ ; *N*-Et-1,3-diazinane-2-thione (EtDiaz)
- (j) 1,3-diazepam-2-thione (Diap)

Scheme 1.

### Experimental

#### Chemicals

$\text{MeOH}$ ,  $\text{Me}_2\text{CO}$  and  $\text{DMSO}-d_6$  were obtained from Fluka Chemical Co. The thione ligands were synthesized according to the literature procedure, by the addition of  $\text{CS}_2$  to diamines in  $\text{Et}_2\text{O}$  and then heating the resulting adduct at  $100^\circ\text{C}$  for 2–3 h, followed by recrystallization from  $\text{MeOH}$  [16, 17]. The ligand, Imt contains 2–3%  $^{15}\text{N}$  labeled nitrogen (a mixture of  $^{15}\text{N}$  labeled and unlabeled diamine was used in preparation of the thione).

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