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# $^{13}$C NMR Studies of the Redox and Exchange Reactions of Gold(I) Thiomalate with Diselenides

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**Exchange reactions of gold(I) thiomalate $(AuStm)_n$ with two diselenides (RSe–SeR), selenocystine and selenocystamine have been studied in $D_2O$ by $^{13}$C NMR spectroscopy. Upon interaction of diselenides with $(AuStm)_n$, the Se–Se bond is broken, resulting in the formation of RSe–Stm and $(AuSeR)_n$ species. RSe–Stm on further decomposition leads to the formation of thiomalic disufide $(Stm)_2$. The second order rate constant was determined for the decomposition of RSe–Stm species and is found to be $3.21 \times 10^{-4}$ l mol$^{-1}$ s$^{-1}$. The intensity of thiomalic disulfide resonances increases, while the intensity of RSe–Stm resonances decreases with time. The end result of both reactions is the formation of $(Stm)_2$ and the deposition of metallic gold and brown ppts. In both cases exchange takes place immediately, however, the overall reaction of $(AuStm)_n$ with selenocystamine was faster than with selenocystine.**

*Keywords*: Gold(I) thiomalate; Diselenide; Selenocystine; Selenocystamine; NMR

## INTRODUCTION

Gold(I) is known to be a strong inhibitor for the catalytic activity of Se-glutathione peroxidase; the only mammalian selenoprotein with a known catalytic activity [1,2]. The complexation of gold(I) thiomalate (Myocrisin), $(AuStm)_n$ with selenium containing amino acids is important, since selenocysteine is present at the active binding site of Se-glutathione peroxidase [3]. The binding of $(AuStm)_n$ with some selenolate ligands, selenopropionate, selenocysteine, selenocystamine and selenoethanoic acid in aqueous solutions has already been reported and it was observed that these ligands replaced all thiomalate from gold(I) forming bis complexes, $[Au(SeR)_2]^-$ [4,5].

$(AuStm)_n$ exists as a polymer in the solid state as well as in solution [6,7]. With its chain structure, it may have a capacity, to react with disufides and diselenides in addition to doing so with thiols and selenols. Since on binding to $(AuStm)_n$, the disulfide (S–S) and diselenide (Se–Se) linkages should be reduced to the thiolate and selenolate forms, respectively, therefore, redox, instead of simple exchange reactions are expected to occur in these interactions. The opening of the S–S linkage by $(AuStm)_n$ has already been reported [8]. The present study

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