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^{31}P NMR STUDIES OF REDOX REACTIONS OF BIS (TRIALKYLPHOSPHINE) GOLD(I) BROMIDE (ALKYL = METHYL, ETHYL) WITH DISULPHIDE AND DISELENIDE LIGANDS

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Redox reactions of bis (trialkylphosphine) gold(I) bromide (alkyl = methyl, ethyl) with two diselenides (R′Se–SeR′), selenocystine and selenocystamine and their corresponding disulfides were studied in D_2O by ^{31}P NMR spectroscopy. Upon interaction of diselenides with $(Me_3P)_2AuBr$ or with $(Et_3P)_2AuBr$, the Se–Se bond is broken, resulting in the formation of R_3PAu^+, R′SeH, R′Se–Au–PR_3, R_3PO and $(AuSeR')_n$. Second-order rate constants were determined for the decomposition of $(R_3P)_2AuBr$. Selenocystamine reacts with $(Et_3P)_2AuBr$ about 100 times faster than its corresponding disulfide. However, cystamine reacts twice as fast with $(Me_3P)_2AuBr$ compared to its corresponding diselenide.

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

INTRODUCTION

Gold(I) compounds are used clinically in the alleviation of symptoms associated with rheumatoid arthritis. This is because they have a high affinity and hence selectivity for –SH and –SeH ligands. It is well known that disodium Au(I) thiomalate (AuStm "Myocrisin") is a potent inhibitor of sulphydryl–disulphide exchange reactions and can participate in facile sulphydryl ligand-exchange reactions. Gold(I) is also known to be a strong inhibitor of the catalytic activity of Se-glutathione peroxidase, the only mammalian selenoprotein with known catalytic activity [1,2].

We are interested in the chemistry of $(Et_3P)_2Au^+$ because it has been reported that orally administered $(Et_3P)_2Au^+$ has similar biological activity to auranofin (a second-generation, orally active gold drug) in the adjuvant-induced arthritic rat model. Recent reviews by McKeage *et al.* [3] and Tiekink [4] show that Et_3PAuCl and other gold(I) phosphine complexes act as potential antitumor agents.

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