ELSEVIER

Inorganic Chemistry Communications 4 (2001) 362–364

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.nl/locate/inoche

Synthesis of cyano(ergothionine)gold(I) complex and its disproportionation in solution

Saeed Ahmad, Anvarhusein A. Isab *

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Abstract

The cyano(ergothionine)gold(I) complex, ErS–Au–CN was prepared and characterized by elemental analysis, IR and NMR spectroscopies. Its disproportionation in solution forming $[Au(CN)_2]^-$ and $[(ErS)_2Au]^+$ was investigated by ^{13}C and ^{15}N NMR. Equilibrium constant (K_{eq}) for disproportionation of the complex was measured by integrating the ^{13}C NMR at 297 K and was found to be 1.08. © 2001 Published by Elsevier Science B.V.

Keywords: Ergothionine; Gold(I); NMR; Disproportionation

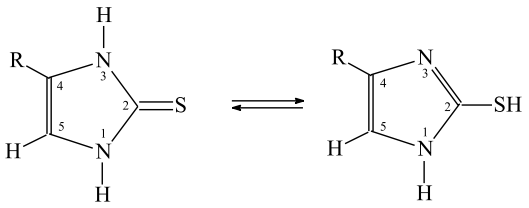
1. Introduction

Disproportionation reactions are characteristics of cyano gold(I) complexes because of a very large formation constant of $[Au(CN)_2]^-$ ($\log\beta = 36.6$) [1], which drives the ligand exchange in forward direction generating $[Au(CN)_2]^-$. Disproportionation reactions have been reported for a variety of cyano(phosphine)gold(I) complexes [2–4]. These complexes are usually monomers and two coordinate in solid state. However, in solution they undergo disproportionation to form the symmetrically substituted complexes according to the equilibrium (1):

$$2[R_3PAuCN] \rightleftarrows [Au(CN)_2]^- + [(R_3P)_2Au]^+ \qquad (1)$$

Recently, we observed that the $[Cy_3P{=}S{-}AuCN]$ [5] and $[Cy_3P{=}Se{-}AuCN]$ [6] type complexes undergo similar disproportionation reactions. Disproportionation is also known for cyano-thiolatogold(I) complexes [7,8]. However, there does not appear to be any study describing disproportionation in cyano(thione)gold(I) complexes, although the synthesis of various cyano(thione)gold(I) complexes has already been reported but without any evidence of disproportionation [9]. The biological significance of such reactions is that they may alter the solution chemistry of gold(I) complexes used in the treatment of rheumatoid arthritis [10–12].

It is well known that gold drugs react with CN^- (produced naturally in the body by oxidation of SCN^- by the enzyme myeloperoxidase in white blood cells [13]) forming the intermediate $[RS{-}Au{-}CN]^-$ which disproportionates to give $[Au(SR)_2]^-$ and $[Au(CN)_2]^-$ species which enter the red blood cells (RBCs) and change the metabolism of gold drugs [10–12]. The level of $[Au(CN)_2]^-$ is higher for smokers than for nonsmokers because of inhalation of HCN from tobacco smoke [14]. The RBCs, which contain thiol and thione ligands, e.g., hemoglobin (Hb), glutathione (Glu) and ergothionine (ErS), can form stable complexes with gold drugs including AuCN [7,11,12]. The concentrations of Hb and Glu in RBCs are 4 and 2.5 mM, respectively, while that of ErS is 0.15–0.60 mM [11]. Glu and Hb have the SH group as their binding site and are more reactive than ErS, which exists in thiol (ErSH), I - thione (ErS), II equilibrium as given by (2). The thione form is predominant in the solid state and at physiological pH [12,15].



(2)

* Corresponding author. Fax: +9663-860-4277.
E-mail address: aisab@kfupm.edu.sa (A.A. Isab).

1387-7003/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S1387-7003(01)00214-3