



Synthesis of cyano(selenone)gold(I) complexes and investigation of their scrambling reactions using ^{13}C and ^{15}N NMR spectroscopy

Saeed Ahmad^a, Anvarhusein A. Isab^{a,*}, Abdul Rahman Al-Arfaj^a, Alan P. Arnold^b

^a Department of Chemistry, King Fahd University of Petroleum and Minerals (KFUPM 1964), Dhahran 31261, Saudi Arabia

^b School of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia

Received 13 March 2002; accepted 27 May 2002

Abstract

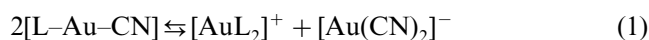
A number of new cyano(selenone)gold(I) complexes have been prepared and characterized by elemental analysis, IR and NMR methods for a series of selenones (imidazolidine-2-selenone and its derivatives or diazinane-2-selenone). It appears from the IR data two of the seven prepared complexes exist as nonionic complexes, [$>\text{C}=\text{Se}-\text{Au}-\text{CN}$] while the remaining five exist as the ionic species, $[\text{Au}(>\text{C}=\text{Se})_2]^+[\text{Au}(\text{CN})_2]^-$ in the solid state. In solution, all complexes are observed to undergo ligand scrambling reactions exhibiting the equilibrium, $2[>\text{C}=\text{Se}-\text{Au}-\text{CN}] \rightleftharpoons [(>\text{C}=\text{Se})_2\text{Au}]^+ + [\text{Au}(\text{CN})_2]^-$. Ligand scrambling reactions of the complexes have been studied in DMSO using ^{13}C and ^{15}N NMR spectroscopy. As a result of the scrambling reaction two sharp resonances are observed in all complexes for both the carbon and nitrogen of CN^- in ^{13}C and ^{15}N NMR, respectively, corresponding to the two equilibrium components, [$>\text{C}=\text{Se}-\text{Au}-\text{CN}$] and $[\text{Au}(\text{CN})_2]^-$. Equilibrium constants (K_{eq}) were determined for the scrambling equilibria by integrating the CN^- resonances in the ^{13}C NMR, recorded at 297 K. K_{eq} values obtained for cyano(selenone)gold(I) complexes are the highest of all the reported values, measured for other complexes.

© 2002 Published by Elsevier Science Ltd.

Keywords: Synthesis; Cyano(selenone)gold(I) complexes; ^{13}C and ^{15}N NMR spectroscopy

1. Introduction

Ligand scrambling reactions shown by Eq. (1) are characteristics of cyanogold(I) complexes ($\text{L}-\text{Au}-\text{CN}$, where L is a soft Lewis base), because of the very large formation constant of $[\text{Au}(\text{CN})_2]^-$, $\log \beta = 36.6$ [1] which drives the reaction in the forward direction generating $[\text{Au}(\text{CN})_2]^-$.



These complexes are usually monomeric and two coordinate in the solid state [2–4] but in solution they undergo disproportionation to form the symmetrically substituted complexes [4–6]. However, tris-(2-cyanoethyl)phosphine (CEP) and *N,N'*-dimethylthiourea (DmTu) form ionic complexes $[\text{Au}(\text{CEP})_2]^+[\text{Au}(\text{CN})_2]^-$ and $[\text{Au}(\text{DmTu})_2]^+[\text{Au}(\text{CN})_2]^-$, respectively, both in solution as well as in the solid state [6–

9]. Ligand scrambling reactions were first observed in cyano-thiolatogold(I) complexes [10] and later, they have been reported for a variety of cyano(phosphine)gold(I) complexes [4–6]. Recently, we observed these reactions in $\text{Cy}_3\text{PSe}-\text{Au}-\text{CN}$ [11], $\text{Cy}_3\text{PS}-\text{Au}-\text{CN}$ [12] (Cy = cyclohexyl) and for a series of cyano(thione)gold(I) complexes [9,13]. The scrambling reactions shown in Eq. (1) are quite important from the biological point of view. Gold drugs used for the treatment of arthritis, react in the body with CN^- and form cyanogold(I) complexes, $[\text{RS}-\text{Au}-\text{CN}]^-$. These complexes undergo facile dissociation leading to the formation of $[\text{Au}(\text{CN})_2]^-$, which enters the red blood cells and changes the metabolism of gold drugs [14–16]. The present report describes the synthesis of several cyanogold(I) complexes with various selenones (imidazolidine-2-selenone and its derivatives or diazinane-2-selenone) and study of their scrambling reactions in DMSO solutions using ^{13}C and ^{15}N NMR spectroscopy. We were also able to measure the equilibrium constants (K_{eq}) for the scrambling of all the complexes by

* Corresponding author. Fax: +966-3-8604277

E-mail address: aisab@kfupm.edu.sa (A.A. Isab).