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

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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, [>C=Se–Au–CN] while the remaining five exist as the ionic species, $[Au(>C=Se)_2]^+[Au(CN)_2]^-$ in the solid state. In solution, all complexes are observed to undergo ligand scrambling reactions exhibiting the equilibrium, $2\,[>C=Se–Au–CN] \leftrightarrows [(>C=Se)_2Au]^+ + [Au(CN)_2]^-$. 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, [>C=Se–Au–CN] and $[Au(CN)_2]^-$. 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.

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 (L–Au–CN, where L is a soft Lewis base), because of the very large formation constant of $[Au(CN)_2]^-$, $\log \beta = 36.6$ [1] which drives the reaction in the forward direction generating $[Au(CN)_2]^-$.

$$2[L–Au–CN] \leftrightarrows [AuL_2]^+ + [Au(CN)_2]^- \quad (1)$$

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 $[Au(CEP)_2]^+$-$[Au(CN)_2]^-$ and $[Au(DmTu)_2]^+[Au(CN)_2]^-$, 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 $Cy_3PSe–Au–CN$ [11], $Cy_3PS–Au–CN$ [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, $[RS–Au–CN]^-$. These complexes undergo facile dissociation leading to the formation of $[Au(CN)_2]^-$, 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

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