

Synthesis and characterization of thiolate–Ag(I) complexes by solid-state and solution NMR and their antimicrobial activity

Anvarhusein A. Isab*, Mohammed I.M. Wazeer

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

Received 2 January 2006; received in revised form 19 February 2006; accepted 2 March 2006

Abstract

Silver(I) complexes of several thiolates have been prepared. These complexes have been characterized by elemental analysis and ^{13}C NMR spectroscopy. All the Ag(I)–thiolate complexes are polymeric in nature. Therefore, ^{13}C CP MAS NMR is being used extensively to analyze the binding site of the ligand and the nature of complexation. A significant shift difference was observed for S binding site whereas smaller shift was observed for carboxylate binding site. The antimicrobial activities for Ag(I)–glutathione complex was measured and compared with Ag(I)–captopril complex.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Thiolates; Silver(I) complexes; CP MAS NMR; Antimicrobial activity

1. Introduction

In recent years there has been a considerable interest in anionic water soluble Ag(I)–complexes with biological activities [1]. As an example of such complexes, bis(thiosulphato)argentite(I) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ (usually called STS), has been known to possess the anti-ethylene property leading to delaying in senescence of ethylene-sensitive flowers such as carnation [2]. Complexes of heterocyclic thiones such as imidazolidine-2-thione (Imt) and diazinane-2-thione (Diaz), and their complexes with transition metals, are of interest in bioinorganic chemistry, because of the search for simple model compounds for metalloproteins. In view of this, Cu(I), Ag(I), Au(I), Hg(II) and Cd(II) complexes with thiones, thioureas have been widely studied in recent years [3–5]. It is known that Ag(I)–thiolate complexes usually form polymeric nature complexes, e.g. Nomiya et al. [6,7] have studied the complexation of thiomalic acid (TMA) with Ag(I) by forming Ag(I)–TMA complex. This complex was polymeric in nature and was characterized by elemental analysis, TG/DTA, FT-IR and ^1H , ^{13}C and ^{109}Ag NMR spectroscopies. They found the formula as $\{\text{NaH}[\text{Ag}(\text{TMA})\cdot 0.5\text{H}_2\text{O}]\}_n$ (where $n = 15\text{--}19$; $M_{\text{W}} = 4320\text{--}5470$).

In this paper, we report the a series of Ag(I)–thiolate complexes of L-cysteine, N-acetyl-L-cysteine, glutathione, penicillamine-methyl ester, N-2-mercapto propionyl glycine, homocysteine, β -D-thioglucose tetraacetate, and ergothionine. All the thiolate complexes seem to be polymeric in nature as none of them is soluble at neutral pH. However, most of the complexes are soluble in the basic media. Since these complexes are soluble at high pH, there is possibility that OH^- may be competing with Ag(I). Still even at high pH, we were not able to observe ^{13}C NMR resonances and in some cases where we were able to observe, they were very broad. Therefore, we decided to employ solid-state NMR. This is probably a first solid-state ^{13}C NMR study where we synthesized series of Ag(I)–thiolate complexes and study them by CP MAS NMR.

2. Experimental

2.1. Chemicals

All the thiol ligands were obtained from the Fluka or Sigma–Aldrich Chemical Companies. The 99.7% D_2O , 36% DCl in D_2O , 40% NaOD in D_2O , and AgNO_3 were also obtained from the Fluka Chemical Co.

2.2. Synthesis of complex and its analysis

Ag(I)–thiolate complexes were prepared as described in the literature [6,8,9]. The products were 60–70% in yield.

* Corresponding author. Tel.: +966 3 860 2645.
E-mail address: aisab@kfupm.edu.sa (A.A. Isab).