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Complexation of gold(I) trimethylphosphine with selenone-containing ligands

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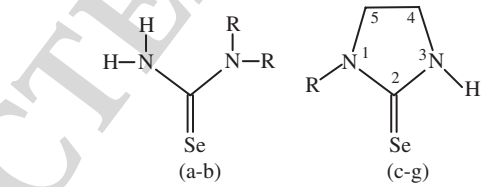
Abstract

Mixed ligand complexes of gold(I) with various selenones and Me_3P, [$Me_3PAuSe{=}C<$]Cl, have been prepared and characterized by elemental analyses, i.r. and n.m.r. methods. A decrease in the i.r. frequency of the >C=Se mode of selenones upon complexation is indicative of selenone binding to gold(I) *via* a selenone group. An upfield shift in ^{13}C-n.m.r. for the >C=Se resonance of selenones and downfield shifts in ^{31}P-n.m.r. for Me_3P moiety are consistent with the selenium coordination to gold(I). The steric effect as well as the basicity of Me_3PAu^+ plays a significant role in bonding with Se-containing ligands compare to the Et_3PAu^+ and Ph_3PAu^+ complexes.

Introduction

The coordination chemistry of gold(I) is of current interest because certain gold(I) thiolate complexes, for example gold(I) thiomalate, gold(I) thioglucose and auranofin (Et_3P–Au–SATg), are found to be potential drugs for the treatment of rheumatoid arthritis [1, 2]. However, the toxicity of gold(I) thiolate complexes is a disadvantage [3]. Recent research has suggested that heavy metal toxicity can be reduced if selenium derivatives are employed [4]. Several reports are available about the spectral and structural characterization of (phosphine)gold(I)–selenium complexes [5–7], but, in order to understand the biochemical mechanism of gold-selenium drugs, more information about the nature of gold-selenium bond is needed [8]. The present report describes the synthesis and characterization of some gold(I) complexes with Me_3P and selenones as ligands. Although we have already reported the synthesis and spectroscopic studies of [Me_3P–Au–Selenourea]$_2Cl_2$ [5], we were interested to see if other selenone complexes give dimeric structures as we obtained for the selenourea (Seu) containing gold (I) complex. We could not obtain crystalline compounds but we measured other spectroscopic studies and compared the data with the reported [$Me_3PAuSeu]_2Cl_2$ complex. The chemistry of these complexes might assist in discovering any salient features, which could conceivably aid in our understanding the role of gold drugs in biological systems. The structures of the selenones used in this study and their resonance assignments are described in Scheme 1.



Scheme 1.

Experimental

Chemicals

Dimethylselenourea (DmSeu), selenourea (Seu), CH_3OD, NH_4NO_3, DMSO-d_6, dimethyl sulfide and all solvents were obtained from Fluka-Aldrich Chemical Co., Germany. Me_3P was obtained from Strem Chemical Co. All the selenones were synthesized according to the procedure described in the literature [9, 10]. Me_3-PAuCl were prepared as described earlier [11].

Synthesis of the complexes

The complexes were prepared by the addition of an equimolar amount of the selenones in acetonitrile to a Me_3PAuCl solution in Me_2Co. After stirring for 15–20 min the resulting colorless solution was filtered and kept in the refrigerator. As a result, white crystalline products were obtained in 50–60% yield. After preparation, the complexes were stored in refrigerator. The elemental analysis of these complexes is given in Table 1.

Spectroscopic measurements

The solid state i.r. spectra of the ligands and their gold(I) complexes were recorded on a Perkin Elmer

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