EXCHANGE REACTIONS BETWEEN ALBUMIN-GOLD(I)-TRIETHYLPHOSPHINE AND Me_3PAuCl OR iPr_3PAuCl STUDIED BY ^{31}P NMR SPECTROSCOPY

Anvarhusein A. Isab, C. Frank Shaw III and Amalia Munoz

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI 53201-0413, USA

The AlbSAuPEt_3 complex was prepared *in vitro* by reacting albumin (AlbSH) with auranofin ($\text{Et}_3\text{PAuSATg}$). The Et_3PAu^+ entity was found to be labile to exchange in the presence of Me_3PAuCl and iPr_3PAuCl . ^{31}P NMR spectroscopy was used to follow these exchange reactions. Either Me_3PAu^+ or iPr_3PAu^+ replaces Et_3PAu^+ from AlbSAuPEt_3 complex. Et_3PAu^+ and R_3PAu^+ ($\text{R} = \text{Me}, \text{iPr}$) were both bound to the weak binding sites (principally histidine) of the protein. Since the iPr_3P ligand is bulkier than Me_3PAu^+ (reflected by its bigger Tollman cone angle) it is surprising that it replaces Et_3PAu^+ almost equally as well as Me_3PAu^+ .

We also demonstrate that Et_3PAu^+ bound to the weak (primarily histidine) binding sites of Cys-34-modified albumin ($(\text{Et}_3\text{PAu})_x\text{AlbS-Acm}$, $\delta\text{P} = \text{ca. } 28 \text{ ppm}$) can be transferred to the Cys-34 of AlbSAuPEt_3 to form the bis complex $\text{AlbS}(\text{AuPEt}_3)_2$ ($\delta\text{P} = 35.7 \text{ ppm}$). The formation of $\text{AlbS}(\text{AuPEt}_3)_2$ shows that the bis complex is indeed in equilibrium with the weak-binding sites characterized by $\delta\text{P} = 28 \text{ ppm}$. The transfer of Et_3PAu^+ between protein species is relevant to mechanisms by which gold may be transferred between proteins *in vivo*.