Potentiometric and NMR studies on palladium(II) complexes of oligoglycines and related ligands with non-co-ordinating side chains.

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Palladium(II) complexes of peptides including Gly-Gly, Gly-Ala, Ala-Gly, Gly-Phe, Phe-Gly, triglycine, Gly-Gly-Ala and tetraglycine were studied by potentiometric and NMR spectroscopic methods. It was found that the reaction of free palladium(II) ion with dipeptides is almost complete below pH 2, therefore pH-metry can not be directly used for stability constant determinations. High excess of chloride ions (0.1 mol dm^{-3}) was used to shift complex formation between $[PdCl_4]^{2-}$ and peptides into the measurable pH range. The formation of the species [PdL(Cl)], $[PdLH_{-1}Cl]^{-}$ and $[PdLH_{-2}]^{-}$ with (NH_2,N^{-},CO_2^{-}) co-ordination was detected with all dipeptides in equimolar solutions. Bis complexes were formed in the presence of an excess of ligand, but their stoichiometry varied as a function of the amino acid sequences of the peptides. In the case of dipeptides with C-terminal Gly residues (X-Gly) the species $[PdL_2H_{-2}]^{2-}$ with 4N co-ordination of two bidentate peptide molecules was formed by the physiological pH, while the stoichiometry of the bis complexes of dipeptides with non-co-ordinating side chains at the C termini (Gly-X) corresponds to $[PdL_2H_{-1}]^{-}$ containing both tridentate and monodentate peptide ligands. Equimolar solutions of palladium(II) and tripeptides are characterized by the formation of the species $[PdLH_{-2}]^{-}$ with $(NH_2,N^{-},N^{-},CO_2^{-})$ co-ordination, while $[PdL_2H_{-2}]^{2-}$ containing two bidentate ligands is the main species in the presence of an excess of tripeptides.

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