Synthesis of Rhenium Carbonyl Derivatives with Glycylglycine as a Ligand

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The importance of metal ions in biological systems is well recognized, and accordingly much attention is paid at present to investigations of the interactions of aminoacids and peptides with different metals [1]. However, there are few reports concerning the synthesis and properties of transition metal carbonyl derivatives with such ligands. It has recently been reported that amino-acids react with carbonly compounds of iron [2], rhodium [3], molybdenum and tungsten [4–6] to produce complexes with aminocarboxylate ligands coordinated with metal atoms, through both the nitrogen atoms of amino-groups and carboxylic oxygen. Previously we have shown [7–9] that similar chelate complexes may be prepared in reactions of some rhenium carbonyl compounds with aminoacids. However, the direct interactions of carbonyl halides of rhenium [7–10] or manganese [11] with aminoacids in boiling dioxane leads to the formation of complexes with aminoacid ligands monodentately coordinated to metal atoms only through their nitrogen atoms.

As far as we know, no reactions of metal carbonyl derivatives with peptides have been investigated. In the present paper we describe the preparation of rhenium carbonyl complexes with glycylglycine as a mono- and bidentate ligand.

Experimental

All operations were carried out in absolute solvents under argon atmosphere. The commercial glycylglycine (Reanal, Hungary) was used. IR-spectra were recorded on IR 75 (Zeiss, Jena) spectrometer, ^{1}H-NMR-spectra were measured with a Tesla BS-467 (60 MHz) instrument.

1. Reaction of $BrRe(CO)_5$ with Glycylglycine

The suspension of $BrRe(CO)_5$ (0.406 g, 1.0 mmol) and glycylglycine (0.265 g, 2.06 mmol) in 30 ml of dioxane was refluxed with stirring for 4 h. The reaction was followed by IR-spectroscopy by the disappearance of ν(CO) bands of $BrRe(CO)_5$. When the reaction was over the resulting light-yellow solution was filtered off, and the uncreacted peptide (0.133 g, 1.06 mmol) was evaporated *in vacuo*. The yellow oil was washed with diethyl ether and dried for 4 h at 80 °C *in vacuo*. The yield of the light-yellow amorphous solid (I) was 0.45 g (83%), m.p. 128–130 °C.

Anal. Calcd. for $C_{11}H_{16}N_2O_8BrRe$: C, 23.16; H, 2.81; N, 4.91; Br, 14.04%. Found: C, 23.19; H, 2.95; N, 5.07; Br, 14.68%.

2. Synthesis of fac-$Re(CO)_3(C_4H_8O_2)$ (glycylglycinate), (II).

a) The suspension of $BrRe(CO)_5$ (0.406 g, 1.0 mmol) and potassium glycylglycinate (0.171 g, 1.0 mmol) in 20 ml of dioxane was refluxed for 4 h. After cooling, the colorless small-crystalline precipitate was filtered off, washed with some water, ethanol and ether and dried *in vacuo*. The yield of (II) was 0.256 g (52%). The product decomposed above 230 °C without melting.

Anal. Calcd. for $C_{11}H_{15}N_2O_8Re$. C, 26.98, H, 3.07; N, 5.72%. Found: C, 26.27; H, 3.07; N, 5.64%.

b) The solution of KOH (0.067 g, 1.2 mmol) in 5 ml of ethanol was added to the boiling solution of (I) (0.570 g, 1.0 mmol) in 20 ml of ethanol. After refluxing with stirring for 3 h, the colorless precipitate was filtered off, washed with some water, ethanol and ether, and dried. The yield of (II), identical with the samples prepared in 2a, was 0.340 g (70%).

Results and Discussion

In contrast to the reactions of α-aminoacids with carbonyl halides of manganese and rhenium yielding bis-aminoacid complexes of the type $XM(CO)_3(NH_2CHRCOOH)_2$ [7–11], only one molecule of glycylglycine enters into the reaction with $BrRe(CO)_5$ in boiling dioxane. The resulting product (I), an amorphous hydroscopic substance, is very stable under normal conditions. It dissolves in most of the polar organic solvents, trifluoroacetic acid and water, and is insoluble in diethyl ether, aliphatic hydrocarbons, benzene and CCl_4. The aqueous solution of (I) has an acidic reaction (pH *ca.* 3.0), and one equivalent of KOH is required for its titration. This suggests the presence in the molecule of (I) of one carboxylic group uncoordinated with the rhenium atom.

The IR-spectrum of (I) shows (in $CHCl_3$ solution) three intensive ν(CO) bands at 2026s, 1906vs and 1882vs cm^{-1}, indicating a *fac*-configuration of carbon monoxide ligands in $Re(CO)_3$ species. There is also (KBr pellets) a band at 1735m cm^{-1}, which belongs to the stretching vibrations of the free COOH group,

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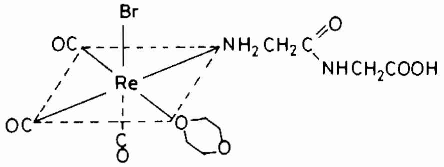
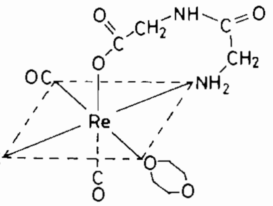
and an intensive broad band at 1626 cm^{-1} (both $\delta(NH_2)$ and vibrations of the peptide CONH-group) [12]. The decreased frequency of $\nu(NH_2)$ vibrations in IR-spectrum of (I) (3260 cm^{-1} compared with 3290 cm^{-1} for potassium glycylglycinate) confirms the coordination of peptide molecules with rhenium atoms through amino-groups.

The ^{1}H-NMR spectrum of (I) (in CF_3COOH solution) shows the signals at δ 7.64 ppm (broad triplet, CON*H*), 4.16 (multiplet) and 3.86 ppm (singlet), both assigned to the protons of two CH_2 and NH_2 groups of the peptide ligand and to those of the dioxane molecule, coordinated with rhenium atom. The presence of dioxane is confirmed by the elemental analysis and also by occurence in the IR-spectrum of (I) of a ν(C–O) band at 1120 cm^{-1}. This band is absent in the IR-spectra of related $BrRe(CO)_3(NH_2CHRCOOH)_2$ complexes, but is observed [7] in that of chelate β-alaninate compound, $Re(CO)_3(C_4H_8O_2)(NH_2CH_2CH_2COO)$.

On the basis of these data, we suppose for (I) the structure with glycylglycine ligand monodentately coordinated with rhenium atom through its amino-group.



(I)



(II)

Both the reaction between $BrRe(CO)_5$ and potassium salt of glycylglycine in boiling dioxane, and the treatment of (I) with ethanolic KOH, lead to the elimination of bromide-anion and formation of new small-crystalline complex (II), decomposing without melting at more than 230 °C. (II) is slightly soluble in chloroform, alcohols, water and trifluoroacetic acid, and insoluble in ethers, aromatic and aliphatic solvents. The aqueous solution of (II) is neutral. The IR-spectrum of (II) in $CHCl_3$ contains three ν(CO) bands at 2020s, 1913vs and 1884vs cm^{-1}. There is no band of the free COOH group in region 1700 cm^{-1}, but present two bands of coordinated with metal carboxylate-anion: ν_{asym} 1605s cm^{-1} and ν_{sym} 1400 cm^{-1}; there is also ν(C–O) band at 1120m cm^{-1} (KBr pellets), assigned to the coordinated dioxane molecule. The ^{1}H-NMR-spectrum of (II) in CF_3COOH solution is very similar to that of (I) and shows the resonances at δ 7.70 (broad triplet), 4.07 (multiplet) and 3.82 (singlet) ppm.

The most probable structure of (II) contains bidentately bound glycylglycinate-anions, coordinated with rhenium atom through both the nitrogen atoms of the amino-groups and carboxylic oxygen.

Previously we have prepared an analogous chelate rhenium carbonyl complex only with β-alaninate-anion as a ligand, whereas the polymeric compounds were produced with salts of α-aminoacids [7]. Apparently, the presence of at least five atoms in the chain of a ligand is necessary for the formation of the chelate cycle in rhenium carbonyl complexes.

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