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Silver(I) Complexes with N-protected Amino Acids

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Although it is well known that metal ions inhibit a number of enzymes, efforts to relate inhibition to the type of protein side chains with which a specific metal or series of metal atoms interact, have been successful only in the case of sulfhydryl groups. In fact the inhibitory effect of mercury(II), cadmium(II), zinc(II), silver(I) and copper(II) ions may be attributable to their interaction with free sulfhydryl groups [1].

Since the chemical basis of enzyme inhibition by silver ions, in absence of free –SH groups, is not well documented and since the detailed knowledge on the interaction of metals with amino acids and peptides, as models for metal–enzyme interactions, may greatly contribute towards rationalizing the enzyme inhibition, in this paper we have studied the silver(I) complexes of some N-protected amino acids, as the N-acetyl- and N-benzoyl-derivatives of glycine, α- and β-alanine, valine, leucine and trypthophan.

The complexes, which have a metal:ligand molar ratio of 1:1, are investigated by means of the infrared spectroscopy. In order to emphasize the amino acid coordination the assignments of the more relevant infrared bands, as reported in Table I, are made by comparing the amino acids, their alkali salts and their deuterated analogues. The coordination sites of the amino acids may be securely evidentiated, as the i.r. spectra of the complexes are very similar in band shape and position to those of the alkali salts. In particular, the NH stretching vibrations of the peptide group do not significantly change in position and the CO ketonic stretching vibrations of the peptide group are shifted at higher energies with respect to those of the alkali salts; all this rules out the participation of these groups in the metal coordination; at the most they are involved in *inter-* or *intra*-molecular hydrogen bonding in crystal packing. This suggests N-protected amino acid coordination with the metal ion through the carboxylate group, in agreement with those previously found for some transition metal ions [2, 3] and with a diminished affinity of the amino group for the metal ion, as, introducing a substituent directly on the amino group, the ligand field of the in-plane donor diminishes.

Trends in positions of and separation ($\Delta\nu$) between antisymmetric and symmetric carboxylate stretching bands provide a useful observation for assigning the coordination type of carboxylate group. In fact in the absence of any strong hydrogen bonding effects, which involve the carboxylate group [4], as the CO bonds become unequivalent a unidentate coordination may be expected to show a large splitting of the carboxylate stretching frequencies, while an asymmetric, symmetric or bridging bidentate coordination must present a small splitting [4–7]. To prevent us from falling into error when a small $\Delta\nu$ separation derives from the presence of strong intramolecular hydrogen bonding in which

TABLE I. More Relevant i.r. Bands (cm^{-1}) and Melting Points (°C) of the Complexes.

	ν(NH)	ν(CO)	$\nu(OCO)_{as}$	$\nu(OCO)_{s}$	$\Delta\nu$	M.P. (°C)
Ag(Acgly)[a]	3300s	1650sh	1595vs	1397vs	198	235–8
Ag(Bzgly)·H_2O	3355m	1625s	1590vs	1382vs	198	350
Ag(Ac-α-ala)	3280m	1640sh	1590vs	1395vs	195	203–8
Ag(Bz-α-ala)	3290m	1633s	1592vs	1393vs	199	200–5
Ag(Ac-β-ala)	3270m	1650s	1570vs	1395vs	175	286–9
Ag(Bz-β-ala)	3290m	1635vs	1565vs	1380vs	175	275–80
Ag(Acval)	3280s	1638s	1592vs	1395vs	197	236–40
Ag(Bzval)	3305m	1635s	1594vs	1398vs	196	216–9
Ag(Acleu)·H_2O	3285m	1645sh	1590vs	1390vs	200	238–42
Ag(Bzleu)	3300m	1630vs	1590vs	1385vs	205	227–30
Ag(Actrp)	3275m	1655sh	1590vs	1395vs	195	195–8

aAbbreviations: Ac = acetyl, Bz = benzoyl, gly = glycine, ala = alanine, val = valine, leu = leucine, trp = tryptophan.

the uncoordinated carboxylate oxygen atom may be involved [5], we have previously suggested also consider the position of the symmetric carboxylate stretching vibration, which is the band directly connected with the oxygen atom linked to the metal; $\nu(OCO)_{sym}$ greater than ~1414 cm^{-1} may be assumed as strongly indicative of bridging bidentate carboxylate, values in the ~1400–1414 cm^{-1} spectral range of monodentate and those lower than ~1400 cm^{-1} of bidentate carboxylate [3]. In particular $\nu(OCO)_{sym}$ at the same or lower energies than that of the corresponding alkali salts is strongly indicative of bidentate carboxylate coordination [3].

On the basis of these considerations in all our silver(I) complexes we may suggest the presence of carboxylate groups which act as bidentate.

Chelation in silver complexes is rare and when coordinated oxygen atoms are present, it also usually involves one sulphur or one nitrogen donor atom [8]. Therefore we may tentatively suggest that in our complexes the bidentate carboxylate coordination may be only apparent, since the two oxygen atoms of the carboxylate group are involved in the coordination of two or more different silver(I) ions, as found in other similar complexes [7, 9, 10], giving rise to polymeric structures, as may be confirmed by their low solubilities and higher melting points.

Experimental

All the complexes were prepared as white precipitates on mixing aqueous or methanolic solution of silver nitrate or silver perchlorate and the sodium salt of the N-protected amino acid.

The analyses of the compounds, performed on a C. Erba Elemental Analyser for C, H and N, well agree the proposed formulas within the experimental error. The infrared spectra of the compounds were recorded on a Perkin Elmer 180 Spectrophotometer as finely divided powders or nujol mulls on KBr pellets as support.

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