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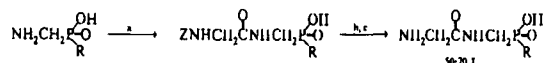
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Synthesis, Crystal Structure and Complexing Properties of Phosphinic Analogues of Glycylglycine

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New phosphinic dipeptides of the general formula $H_2NCH_2CONHCH_2P(R)(O)(OH)$ where $R=Me, Ph$ and $t-Bu$ has been synthesized from the free phosphinic acids and N-hydroxy succinimide esters of the N-protected glycine. The deprotected dipeptides were purified by combination of the column chromatography on strong and weak cation exchange resins by elution with diluted aqueous ammonia (0.1-3%).



Reagents: a-Boc- or Z-Gly-Succ, $H_2O/EtOH=1:1$, $NaHCO_3$, $0^\circ C$ 1h, RT 12h; b-HBr/AcOH or HCl/aq. c (purification) - 1. Dowex 50; 2. Amberlite CG 50; elution by water or diluted ammonia

Crystal structure determination of the phenylphosphinic dipeptide confirmed zwitterionic structure expected in the solid state. Bond distances and angles in peptide moiety are virtually the same as in common dipeptides and therefore, are not influenced by the phosphinic group. The molecule in the crystals are connected by extensive hydrogen bonds into hydrophilic and hydrophobic layers. Dissociation constants pK_A were determined pH-metrically ($25^\circ C$, $I=0.1M$ (KNO_3)). The constants were determined for GlyAMP^{34a} (1.721(4), 8.026(3)) and for GlyAMP^{34b} (1.240(8), 7.997(4)) and these values correspond to the expected electron withdrawing ability of phosphinic moiety. The stability constants $\log \beta_{pwr}$ of Cu(II) complexes with the phosphinodipeptides, GlyGly and GlyAMP, $\beta_{pwr} = [H_p L_q M_n] / [H^+]^p [L^-]^q [M]^n$, are list in the Table:

p	q	r	GlyAMP ^{34a}	GlyAMP ^{34b}	GlyGly	GlyAMP
1	1	1	9.19(9)			11.98
0	1	1	5.55(2)	5.46(2)	5.55	6.55
-1	1	1	0.160(8)	-0.122(8)	1.40	1.64
-2	1	1	-9.01(1)	-9.35(1)	10.71	-6.71
-3	1	1	-21.30(3)			
-1	2	1	3.13(4)	3.01(8)	4.54	4.89
-2	2	1	-6.25(6)	-6.5(1)	≈7.4	
pK_A pept. amide			5.39	5.58	4.15	4.91

The models presented were found by computation ("trial and error" method) of many thousands models using the OPTUM - a new program for the determination of equilibrium constants¹.

References

- [1] M. Kývala, I. Lukeš: CHEMOMETRICS 95, Pardubice, Czech Republic, Abstract Book p.63