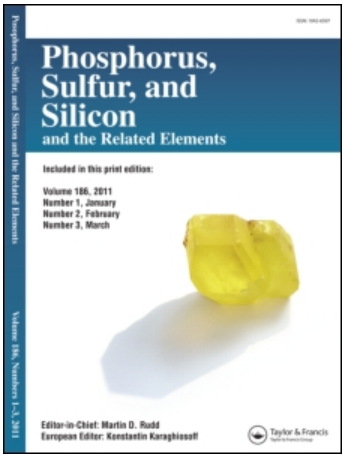


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# Synthesis, Crystal Structure and Complexing Properties of Phosphinic Analogues of Glycylglycine

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

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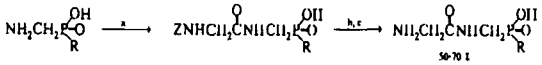
New phosphinic dipeptides of the general formula $H_2NCH_2CONHCH_2P(R)(O)(OH)$ where R=Me,Ph and *t*-Bu has been synthetized from the free phosphinic acids and N-hydroxysuccinimide esters of the N-protected glycine. The deprotected dipeptides were purified by combination of the column chromatography 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°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 angels 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 °C, I=0.1M ($KNO_3$)). The constants were determined for $GlyAMP^{Me}$ (1.721(4), 8.026(3)) and for $GlyAMP^{Ph}$ (1.240(8), 7.997(4)) and these values correspond to the expected electron withdrawing ability of phosphinic moiety. The stability constants $\log\beta_{pqr}$ of Cu(II) complexes with the phosphinodipeptides, GlyGly and GlyAMP; $\beta_{pqr} = [H_pL_qM_r] / [H^+]^p [L]^q [M]^r$, are list in the Table:

| p | q | r | $GlyAMP^{Me}$ | $GlyAMP^{Ph}$ | 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 OPIUM - a new program for the determination of equilibrium constants[1].

## *References*

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