## Multinuclear NMR and Potentiometric Studies on the Interaction of Zinc and Cadmium With Cytidine and Glycylglycine. The Effect of the Anion\*

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## ABSTRACT

The stability constants for binary complexes formed between Zn<sup>2+</sup> and Cd<sup>2+</sup> with cytidine and glycylglycine and for the ternary complexes with the same ligands were determined by spectroscopic (<sup>1</sup>H and <sup>13</sup>C NMR) and, except those involving Zn<sup>2+</sup> and cytidine, by potentiometric pH titrations in aqueous solution. The calculated values show that cadmium binds much more strongly to cytidine than zinc, and that a small but significant increase in the stability of zinc/cytidine interaction, but not for cadmium/cytidine, is observed in the presence of glycylglycine. The chemical shifts observed for cytidine with zinc show a marked dependence on the anion, being much larger for the chloride salt than for the nitrate and increase upon addition of glycylglycine, although the calculated stability constants are identical for both salts. Finally, the choice of reference chemical shifts used in the spectroscopic titrations and the effect of charged species on the values of the acidity constants are discussed.

## INTRODUCTION

The recognition of the active role of zinc in the enzymatic activity of several enzymes has spurred an enormous interest in the biological role of this metal. Several DNA-dependent RNA polymerases were shown to be zinc metalloenzymes and recently it was claimed that they possess a specific binding site for purine

<sup>\*</sup> Effects of salts on <sup>1</sup>H and <sup>13</sup>C NMR spectra (supplementary material) is available from Dr. de Castro. Address reprint requests to: Dr. Baltazar de Castro, Departamento de Química, Faculdade de Ciências do Porto, 4000 Porto, Portugal.