

A Voyage In The B Vitamins World: B₆ As Novel Ligand In Cluster Chemistry And New Discoveries In The Field Of B₁₂ Crystallography.

N. Marino,^{1,2} D. Armentano¹, G. De Munno,¹ R. P. Doyle²

¹Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Italy

³Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100, United States

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E-mail: nadia.marino@unical.it; nmarino@syr.edu

Presented herein are a couple of crystallographically interesting examples (small molecule *vs.* 'large' small molecule) featuring either vitamin B₆ (pyridoxine, PN-H) or B₁₂ (cyanocobalamin, CNCbl), the former as novel and versatile ligand in cluster chemistry, and the latter in a unique protonated form offering up the occasion to examine and discuss the influence of crystal packing forces in cobalamins' structures. In particular:

I. By using vitamin B₆ in its mono-deprotonated pyridoxine form (PN-H⁻) [PN = 3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine], we have synthesized and magneto-structurally characterized two tetranuclear Mn^{II}₂Mn^{III}₂ and Cu^{II}₄ compounds of formula [Mn₄(PN-H)₄(CH₃CO₂)₃Cl₂]Cl·2CH₃OH·2H₂O and [Cu₄(PN-H)₄Cl₂(H₂O)₂]Cl₂, showing the ability of B₆ to act as unusual but suitable ligand toward the self-assembling of cubane moieties [1].

II. In the course of experiments directed toward the synthesis of vitamin B₁₂-bioconjugates for drug-delivery purposes, we observed the formation of well-shaped red parallelepipeds from a concentrated aqueous solution of the HPLC-purified vitamin. The crystals were investigated classically by using MoK_α radiation at 98 K, and they turned out to be an unprecedented CNCbl-trifluoroacetate salt. By comparing this structure with other CNCbls reported in the literature, we noted significant differences in the upward fold angle of the corrin macrocycle, which could only be justified by assuming the existence of a strong relationship between crystal packing forces and cobalamins' molecular structure, as mostly ignored in the field of B₁₂ crystallography so far [2].

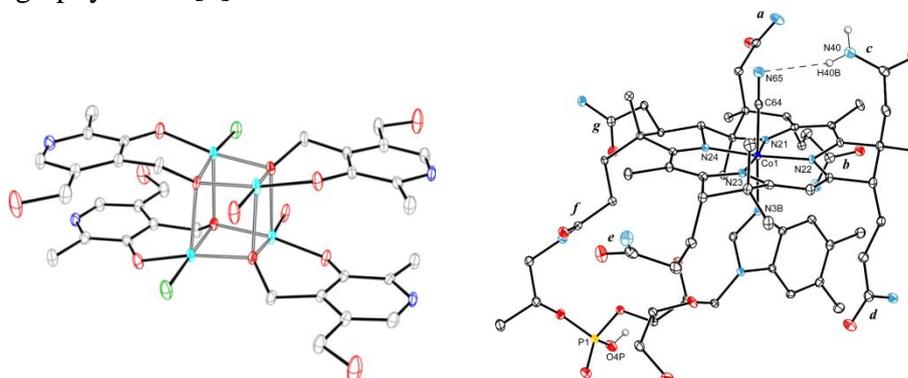


Figure 1: Left. A view of the cationic unit in complex [Cu₄(PN-H)₄Cl₂(H₂O)₂]Cl₂; H-atoms omitted for clarity. Right. A view of the isolated CNCbl(H)⁺ cation.

References

1. N. Marino, D. Armentano, T.F. Mastropietro, M. Julve, G. De Munno, J. Martínez-Lillo, *in prep for Cryst. Growth Des.* (2013).
2. N. Marino, A. E. Rabideau, R. P. Doyle, *Inorg. Chem.* **2011**, 50, 220-230.