

## AVVISO DI SEMINARIO

**GIOVEDÌ 19 LUGLIO 2007 alle ore 16.00**

nell'aula A1 del Dipartimento di Scienze Chimiche

il prof. **Pawel M. Kozlowski**

Department of Chemistry, University of Louisville, Kentucky, USA

terra' una conferenza dal titolo:

**"QUANTUM CHEMICAL MODELLING OF CO-C BOND  
ACTIVATION IN B<sub>12</sub>-DEPENDENT ENZYMES"**

Tutti gli interessati sono invitati a partecipare.

**Il Direttore**

**Prof. Lucio Randaccio**

### SOMMARIO

The origin of the enormous catalytic activity of coenzyme B<sub>12</sub>-dependent enzymes continues to be an outstanding problem in bioinorganic chemistry. During enzymatic catalysis the Co-C bond of coenzyme B<sub>12</sub> (AdoCbl) is cleaved homolytically, leading to the formation of the 5'-deoxyadenosyl radical and cob(II)alamin. The rate of enzymatically accelerated homolytic cobalt-carbon bond cleavage of AdoCbl exceeds the rate observed in aqueous solution by about 12 orders of magnitude as a consequence of the coenzyme interaction with the substrate in the presence of apoenzyme. Despite the great effort that has been devoted to this problem, the mechanism of the catalytic activation is poorly understood. To the extent it has been addressed experimentally, evidence from model systems indicate that steric hindrance around coordinated alkyl ligands leads to a higher homolysis rate. Different models have been suggested, but none can be considered as fully satisfactory in light of a large body of experimental results.

Recent progress in computational modeling of the catalytic activation of cobalt-carbon bond cleavage will be summarized. The growing interest in modeling the structure and electronic properties of AdoCbl has demonstrated that computer simulations, in particular density functional theory (DFT) can be an important part of coenzyme B<sub>12</sub> research.