Charge Density Studies of the Ni(II) Complex as a Chiral Synthon

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Metal complexes of Schiff bases of amino acids can be utilized in asymmetric syntheses of both multi-ton industrial production of amino acids and special commercially unavailable non-coded ones as well. Our efforts in catalytic asymmetric synthesis of alpha-amino acids are concentrated on nickel(II) complexes of Schiff bases of (S)-N-benzylproline (2-benzoylphenyl)amide and alpha-amino acids [1,2]. Previously, a combination of solution NMR, solid state NMR, X-ray crystallography and DFT calculations [3] was used to disclose the nature of the asymmetric induction achieved with chiral nickel complexes. The donation of electron density from the π-system of the benzyl ring to nickel orbitals was identified as important factor which might be used for creation of synthons with higher asymmetric induction. DFT B3LYP calculations confirmed a weak interaction, which shortens the distance between the benzyl plane and the nickel atom [3].

In order to examine the experimental charge density on above crystal and to prove the hypothesis on the relation between the interaction mentioned and the yield of asymmetric syntheses, the high resolution single crystal X-ray diffraction experiments (λ = 0.5604 Å) at low temperature (100 K) with synchrotron radiation at the beamline F1 with a CCD area detector was done. Integration, data reduction and absorption correction was done by Bruker software SAINT6.26, SADABS2.0 and XPREP. Preliminary results of the multipole refinement based based on 86 437 reflections (20 280 unique, -21 ≤ h ≤ 21, -22 ≤ k ≤ 22, -59 ≤ h ≤ 59, 9_max = 42.4°) are presented. Starting parameters for multipole refinement were taken from SHELXL97 results (R1 = 0.0336) and all calculations were carried out on F2 using XD [4] suite of programs.

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Figure 1:
Static electron deformation densities in the plane defined by the atoms Ni(1), N(2), and N(6).

References