04. ATOMIC SCALE MECHANISM AND CHEMICAL PROPERTIES

04.1-10 CRYSTAL STRUCTURE RELATIONSHIPS BETWEEN CYCLOOCTAADIENE COMPLEXES OF Pt(II). By F. M. Muslu, Dpto. Q. Inorgánica. Colegio Universitario de Alava (UPV), VITORIA and S. Garcia-Blanco. Dpto. Rayos-X, Instituto Rocasolano, CSIC, Serrano 119, MADRID-6, SPAIN.

The crystal structures of $C_8H_8PtX_2$ complexes (where $X = Cl, Br, I$ and SCN ) have been determined by X-ray diffraction. The crystallographic data are as follows:

Formulas $C_8H_8PtCl_2$ $C_8H_8PtBr_2$ $C_8H_8PtI_2$ $C_8H_8Pt(SCN)_2$

S. Group $P2_1_2_1_2$ $F4_1_2_1_1$ $P2_1/n$ $Pna2_1$

a (Å) 12.3109(10) 12.4636(20) 12.338(5) 16.876(4)
b 10.9748(10) 11.1762(20) 10.8926(3) 9.0921(8)
c 6.9220(5) 7.0747(9) 8.2958(3) 7.5982(7)

These complexes are compared against those found in the bibliography of formulae $C_8H_8XY$ (where $M = Pt, Pd$ and Rh).

The comparison is made in terms of: a) metal coordination and b) bond and interatomic distances, bond angles and torsion angles, with respect to that of free cyclooctaadiene ring.

04.1-17 THE CONFORMATION OF PROLINE USING THE CONCEPT OF PSEUDOROTATION. By K.K. Chacko, Veena Srinivasachar and S. Swaminathan, Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras – 600 025, India.

Conformational analysis of proline based on the usual best plane method is only an approximate way of defining its true conformation. A more rigorous approach is to use the concept of pseudorotation applied to the five membered pyrroolidine ring system. The procedure for the calculation of the pseudorotational parameters $\theta^*$ (Plane angle) and $\theta^+$ (maximum amplitude of puckering) from the endo/cyclic torsion angles of the ring system and the method of representation of its conformation by making use of the pseudorotational pathway chart are already available (Chacko, Swaminathan and Veena (1985) Curr. Sci., 22, 660).

Here we make use of the crystallographic data (from the Cambridge Data file) consisting of over 120 prolyl residues in peptides and cyclic peptides to carry out a detailed analysis on the conformation of proline using the concept of pseudorotation. The results of the analysis bring out the salient features of the mode of puckering of the pyrroolidine ring system will be presented.

04.2-1 DEFORMATION OF $\gamma$-ELECTRON SYSTEMS. By K.C. Watson. Department of Chemistry, Texas Christian University, Fort Worth, Texas USA.

The stereoselectivity and accelerated rates of reaction of norbornene and related systems has been shown to be associated with a deformation of the $\gamma$-electron system. The nominally sp$^2$ hybridized carbon atoms are pyramidalized, which results in the $\gamma$-system deviating from planarity by bending hinge-like along the C-C bond. In $\gamma$-sesquisubstituted norbornenes and its derivatives the driving force for the pyramidalization has been attributed to ground state torsional effects, antihyperconjugative interactions between $\pi$ and "cyclopentane ribbon" orbitals and to anti hyperconjugative effects between the $\gamma$-system and specific $\sigma$ bonds. It has been impossible to experimentally distinguish between these effects.

In general, anti-sesquisubstituted norbornene is expected to be planar because the above effects are cancelled due to symmetry. However, if half of the anti-sesquisubstituted norbornene system is modified an asymmetry is introduced and the magnitudes of the above effects might be evaluated. In addition to the structures already in the literature, we will report on a low temperature investigation of anti-sesquisubstituted norbornene, several derivatives in which the ethylene bridge has been modified by substitution and on several $\gamma$-oxabenzansesquisubstituted norbornene structures. The results of molecular mechanics and quantum mechanical calculations will be compared with the experimental data.