

04.1-16 CRYSTAL STRUCTURE RELATIONSHIPS BETWEEN CYCLO OCTADIENE COMPLEXES OF Pt(II). By F. Mz. Musitu. 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  $C_8H_{12}PtX_2$  complexes ( where  $X = Cl, Br, I$  and  $SCN$  ) have been determined by X-ray diffraction.

The crystallographic data are as follow:

| Formulae      | $C_8H_{12}PtCl_2$ | $C_8H_{12}PtBr_2$ | $C_8H_{12}PtI_2$ | $C_8H_{12}Pt(SCN)_2$ |
|---------------|-------------------|-------------------|------------------|----------------------|
| S. Group      | $P2_12_12_1$      | $P2_12_12_1$      | $P2/n$           | $Pna2_1$             |
| a (Å)         | 12.3109(10)       | 12.4636(20)       | 12.9384(5)       | 16.8764(26)          |
| 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)            |
| $\beta^\circ$ | 90                | 90                | 106.90(3)        | 90                   |

These complexes are compared against those found in the bibliography of formulae  $C_8H_{12}MXY$  (where  $M = Pt, Pd$  and  $Rh$ ). This comparison is made in terms of : a) metal coordination and b) bond and intraannular distances, bond angles and torsion angles, with respect to that of free cyclooctadiene ring.

04.1-17 THE CONFORMATION OF PROLINE USING THE CONCEPT OF PSEUDOROTATION. By K.K.Chacko, Veena Ravichandran 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 pyrrolidine ring system. The procedure for the calculation of the pseudorotational parameters 'P' (Phase angle) and ' $\theta$ ' (maximum amplitude of pucker) from the  $\theta$  endocyclic 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 (1983) Curr. Sci., 52, 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 bringing out the salient features of the mode of puckering of the pyrrolidine ring system will be presented.

04.2-1 DEFORMATION OF  $\pi$ -ELECTRON SYSTEMS. By W.H. 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  $\pi$ -electron system. The nominally  $sp^2$  hybridized carbon atoms are pyramidalized, which results in the  $\pi$ -system deviating from planarity by bending hinge-like along the C-C bond. In *syn*-sesquinorbornene 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 antihyperconjugative effects between the  $\pi$ -system and specific  $\sigma$  bonds. It has been impossible to experimentally distinguish between these effects.

In general, *anti*-sesquinorbornene is expected to be planar because the above effects are cancelled due to symmetry. However, if half of the *anti*-sesquinorbornene 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*-sesquinorbornene, several derivatives in which the ethylene bridge has been modified by substitution and on several *syn*-oxabenzosesequinorbornene structures. The results of molecular mechanics and quantum mechanical calculations will be compared with the experimental data.

04.2-2 ANGULAR PREFERENCES OF INTERMOLECULAR FORCES AROUND HALOGEN CENTERS: DIRECTIONAL ANISOTROPY OF "ELECTROPHILIC AND "NUCLEOPHILIC" APPROACH AROUND HALOGENS AND "ELECTROPHILE-NUCLEOPHILE" PAIRING IN HALOGEN...HALOGEN INTERACTIONS. By N. Ramasubbu and R. Parthasarathy, Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14263, USA.

During our studies of  $Se \cdots Se$  interactions in diselenides (Ramasubbu and Parthasarathy (1983) Amer. Cryst. Assn. Series 2, 11, pc8), we noticed that halogen atom X of a few R-X groups engage in two types of contacts: (i) with Se in a "head-on" fashion i.e., the Se atom approaches X on the back-side of the R-X bond and the selenide plane normal to R-X and (ii) "side-on" fashion when Se approaches X nearly normal to the R-X bond, and X approaches Se along the backside of Y-Se or Z-Se of selenides. These results suggested preferred direction of "electrophile" (E) and "nucleophile" (Nu) approach around halogen centers. Hence, we analyzed the crystallographic environment of halogen centers (C-X, X = Cl, Br, I) (Murray-Rust and Motherwell (1979) J. Am. Chem. Soc. 101, 4374) using structural data contained in the Cambridge Crystallographic Data Base and locally modified version of GEOM78. We limited our analysis to monovalent halogens of the C-X group and to distances equal to or less than the sum of the van der Waals' radii of contacting atoms. We also focused on "strong interactions" showing the closest approach ( $\Delta r$  is most,  $\Delta r_{Nu} = r_X + r_{Nu} - d_{X \cdots Nu}$ ;  $\Delta r_E = r_X + r_E - d_{X \cdots E}$ ;  $\Delta r_X = 2r_X - d_{X \cdots X}$ ) assuming that weaker interactions to the same halogen atom are consequences of the stronger ones. We find that, in general, "electrophiles" tend to approach the halogen centers at an angle  $\theta(C-X \cdots E)$  approximately equal to  $90^\circ$  and "nucleophiles" at  $\approx 180^\circ$ . When there are no dominant interactions of X with an "electrophile" or a "nucleophile" ( $\Delta r_{Nu}$  or  $\Delta r_E < \Delta r_X$ )  $C_1-X_1 \cdots X_2-C_2$  interactions fall into two groups: (a) Types I and II with "electrophile-nucleophile" pairing as