

PS09.01.16 CHARGE DENSITY ANALYSIS IN THE 3d-METAL SANDWICH COMPLEXES WITH THE MIXED-RING π -LIGANDS. K.A.Lyssenko*, M.Yu. Antipin*, S.Yu.Ketkov** Institute of Organoelement Compounds (INEOS), Vavilov St. 28, B-334, Moscow, 117813, Russia. ** Institute of Organometallic Chemistry, N.Novgorod, 603600, Russia.

Electron density distribution using single crystal X-ray diffraction data was studied for the similar π -complexes (η^5 -C₅H₅)M(η^7 -C₇H₇) where M=Ti, V and Cr. This series represents the 16-, 17- and 18-electron complexes, respectively. Crystal structures studied are isomorphous and compounds are isostructural (space group Pmna, Z=4, molecules in crystals have m-symmetry), that allows to compare carefully their molecular geometry and electron density distribution features caused mainly by the different nature of the transition metal. All experimental data were obtained at low temperatures (100-150K) with the "Siemens P3/PC" diffractometer using Mo-radiation, for each crystal ca. 15000 reflections were collected, and R values were 0.025-0.030. Similar crystal structure has the 17- electron complex (η^5 -C₅H₅)Ti(η^8 -C₈H₈) that was also studied (data collection at 203K because of the phase transition, ca 9000 reflections, R=0.025). All complexes have the sandwich-like structure with the planar cyclic ligands that are symmetrically bonded with the metal atoms. A typical asymmetry of the electron density distribution picture near the metals was observed in the deformation electron density maps for all compounds studied that was attributed to the different occupancies of the 3d-metal orbitals. Numerical values of these occupancies were estimated using a multipole refinement procedure. In the series of the 16-, 17-, 18-electron complexes a gradual occupancy of the different metal orbitals was observed that was in agreement with the performed ab initio calculations and measured vapor-phase electronic absorption spectra of the compounds studied. It was found for Ti-complexes with the C₇H₇- and C₈H₈-ligands that due to the different size of the ligand ring the energy sequence of the molecular e₁, a₁ and e₂ orbitals has been changed, and this effect is clearly seen in the deformation electron density maps.

PS09.01.17 ELECTRON DENSITY STUDIES ON TETRAAQUABIS (HYDROGENMALEATE)IRON(II). Isolda M. de C. Mendes & Nelson G. Fernandes. Department of Chemistry, Federal University of Minas Gerais, CP702-31270 901- Belo Horizonte, Brazil

The non-spherical distribution of the valence electrons in a crystal of Fe(C₄H₃O₄)₄H₂O was investigated according to the Hirshfeld deformation refinement, as part of a study of short hydrogen bonds in compounds of divalent transition metals with maleic acid.

X-ray data were collected on a Siemens four-circle diffractometer at 298 K, by the ω -2 θ scan technique, using MoK α radiation up to $\sin\theta/\lambda=1.20 \text{ \AA}^{-1}$. For a P1 space group, 8131 reflections were measured which resulted in 6461 unique reflections (R_{int}=0.0085), all of them were considered as observed in subsequent refinements, based on F² with applied extinction correction. For deformation refinement, 260 parameters, R=0.0299, wR=0.0277 against the conventional refinement, 126 parameters, R=0.0495, wR=0.0474.

In the maleate ligand the two carbonyl groups are linked by a short quasi-linear hydrogen bond with an O...O' distance of 2.428(1) Å. The asymmetric crystallographic environment on this bond is revealed by the different O...H distances and electron density maxima of 1.09(2) Å and 0.2 eÅ⁻³ for the shorter and 1.35(2) Å and 0.1 eÅ⁻³ for the longer bond. Both maxima are at a distance of ~0.7 Å from the oxygen atoms. Density maps show that one of C...O bonds is significantly shorter and with an electron density maximum twice higher than any other of these bonds. Six oxygen atoms form an octahedron around iron atom, the assumed local symmetry is 4/mmm.

In this case, the maps reveal an aspherical density distribution with maxima of ~0.2 eÅ⁻³ and ~0.3 eÅ⁻³ directed between the vertices of the octahedron.

PS09.01.18 THE CHARGE DENSITY IN ADENOSINE AT 123K. H. W. Yang, J. R. Ruble, W. T. Klooster, S. K. Kampermann, B. M. Craven, Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260

New X-ray diffraction data for adenosine (C₁₀H₁₃N₅O₄) have been collected at high resolution ($\sin\theta/\lambda < 1.34 \text{ \AA}^{-1}$) and reduced temperature (123K). The structure has been refined by least squares using Stewart's rigid pseudoatom model. All nuclear positional and anisotropic m. s. displacement parameters were assigned fixed values from a previous neutron diffraction study at 123K (1). Thus the least squares refinement involved only the scale factor, an isotropic extinction parameter, three κ radial parameters (for C, N and O), and 356 pseudoatom electron population parameters. The refinement, which was based on F² and included all 10,083 reflections, gave R(F²) = 0.046 and R_w(F²) = 0.077 with goodness-of-fit = 1.64.

The total electronic charge density in the crystal $\rho(r)$, has been mapped for pseudoatoms at rest. Also the Laplacian of the charge density $\nabla^2\rho(r)$ has been analysed at the (3, -1) bond critical points (2). At the bond critical points, $\rho(r)$ is consistently greater in the adenine base than in the ribose sugar. Thus C4-C5 and C5-C6 in adenine ring system have $\rho(r) = 2.05(7)$, $2.02(7)e\text{\AA}^{-3}$, whereas C1'-C2' and C2'-C3' in the ribose ring have $\rho(r) = 1.78(6)$, $1.67(5)e\text{\AA}^{-3}$. Also, the Hessian matrix at the bond critical points indicates considerable double bond character for C4-C5 and C5-C6 ($\epsilon = 0.43$, 0.43) whereas this is lacking for C1'-C2' and C2'-C3' ($\epsilon = 0.09$, 0.12). The Laplacian at all H-bond critical points is positive, indicating a lack of covalent bonding. There is a weak H bond, C2-H2...O2'.

Work supported by a grant GM-39513 from NIH.

(1) W. T. Klooster, J. R. Ruble, B. M. Craven and R. K. McMullan (1991). *Acta Cryst.*, **B47**, 376-383.

(2) R. F. W. Bader (1991). "Atoms in Molecules, A Quantum Theory." Clarendon Press, Oxford. Chap. 2.

PS09.01.19 EXPERIMENTAL CHARGE DENSITY OF DL-SERINE AND L-SERINE. J. Buschmann, T. Koritsánszky, M. Ramm, P. Luger, Institute for Crystallography, Free University of Berlin, Germany

Full topological analyses /1/ of the electron density of the racemic and the nonracemic form of serine will be presented. This investigation is part of a project where the electronic properties of amino acids are to be determined, using Bader's approach /1/, from the experimental density calculated with the multipole program package XD /2/.

Reflection intensity data were collected up to a limit of $(\sin\theta)/\lambda = 1.18 \text{ \AA}^{-1}$ on a SIEMENS 4-circle X-ray diffractometer with MoK α radiation at a temperature of 150°C which was maintained by a nitrogen gas stream cooling device.

DL-serine: monoclinic, P2₁/a, Z=4, 10515 reflections measured, 3081 independent observed reflections, conventional refinement $r_w = 0.029$;

L-serine: orthorhombic, P2₁2₁2₁, Z=4, 7766 reflections measured, 2910 independent observed reflections, conventional refinement $r_w = 0.030$.

The L-forms of the molecule in the two different crystal structures are alike, showing the same overall conformation, but only the DL-serine crystal structure possesses a strong intermolecular hydrogen bond. So this is a special situation to look for the transferability of multipole parameters and the dependency of electronic and topological properties on intra- and intermolecular interactions.

/1/ R. F. W. Bader, "Atoms in Molecules, Clarendon Press, Oxford, 1994.

/2/ T. Koritsánszky et al.: XD, A Computer Program Package for Refinement and Analysis of Charge Densities from X-Ray Diffraction Data, Free University of Berlin, 1995.