

of the complexes has been investigated by theoretical calculations[2], but is still in controversy. Here we show the bonding nature of the 1-zirconacyclopent-3-yne complex by means of experimental charge density analysis.

Diffraction data were collected using synchrotron radiations at KEK PF-AR NW2 beam line by Rigaku Mercury CCD diffractometer up to $\sin\theta/\lambda = 1.0 \text{ \AA}^{-1}$. Multipole expansion method was applied for modeling of atoms. Final R was 0.027 for reflections with $I > 1.5\sigma(I)$.

The 1-zirconacyclopent-3-yne moiety is planar. Valence shell charge concentrating region on each of the C atoms on the α positions extends toward the charge depressing regions on the Zr atom. Bond critical points and bond paths were found on the Zr-C(α) bonds. The bond paths curve inwardly near the C(α) atoms. These suggest that both of the η^2 - σ , σ and η^4 - π , π structures contribute to the bonding. No bond paths, in contrast, were found on the Zr-C(β) bonds. In conclusion, bonding of 1-zirconacyclopent-3-yne is in resonance between η^2 - σ , σ and η^4 - π , π structures.

[1] a) Suzuki N. *et al.*, *Science*, 2002, **295**, 660; b) Suzuki N. *et al.*, *J. Am. Chem. Soc.*, 2004, **126**, 60. [2] a) Lam K. C., Lin, Z., *Organometallics*, 2003, **22**, 3466; b) Jemmis E. D. *et al.*, *Organometallics*, 2003, **22**, 4958.

Keywords: charge density, chemical bonding, zirconium compounds

P.14.07.9

Acta Cryst. (2005). A61, C427

Different Approaches to Absorption Corrections for Charge Density Analyses

Jozef Kožišek^a, Martin Breza^a, Hartmut Fuess^b, Robert H. Blessing^c,
^aDepartment of Physical Chemistry, Slovak University of Technology, Bratislava, Slovakia. ^bMaterials Science, Darmstadt University of Technology, Darmstadt, Germany. ^cHauptman-Woodward Medical Research Institute, Buffalo, New York, U.S.A. E-mail: jozef.kozisek@stuba.sk

In order to increase the accuracy of high-angle diffraction data for multipole refinement with XD, crystals with diameters of up to 0.5 mm were measured. Bigger crystals give intensity data with higher signal-to-noise ratios, especially for high-angle reflections, but large crystals also make accurate absorption and extinction corrections a necessity, especially for crystals of 3d-coordination compounds. Extinction corrections require values of TBAR, the absorption-weighted mean sum of incident and diffracted beam path lengths through the crystal, and anisotropic extinction corrections require also the direction cosines of the incident and diffracted beams [1].

Several absorption correction methods were compared based on crystallographic R-values, maximum and minimum values of residual densities, and the d -orbital populations from the experimental electron density studies of several 3d-coordination compounds [2-3]. Valuable additional information was obtained from quantum chemical calculations and subsequent topological analysis of both experimental and theoretical electron densities [4].

[1] Blessing R. H., *J. Appl. Crystallogr.*, 1997, **30**, 421. [2] Kožišek J., Fronc M., Skubák P., Popkov A., Breza M., Fuess H., Paulmann C., *Acta Cryst.*, 2004, **A60**, 510. [3] Kožišek J., Hansen N.K., Fuess H., *Acta Cryst.*, 2002, **B58**, 463. [4] Májek P., Brudíková K., Breza M., *J. Mol.Struct. (Theochem)*, 2004, **711**, 115.

Keywords: charge density, copper compounds, properties

P.14.07.10

Acta Cryst. (2005). A61, C427

Chemical Bonding Based on Charge Density Calculations for Solids

Karlheinz Schwarz, Peter Blaha, *Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.* E-mail: kschwarz@theochem.tuwien.ac.at

We calculate the electronic structure of solids within density functional theory (DFT) and use the WIEN2k code [1] that is based on the full-potential augmented plane wave (APW) method. The key quantity is the electron density, which can be decomposed into contributions according to core and valence regions or even a small

energy region (an energy sub band) that gives more insight into the chemical bonding than the total density. The partial densities of states (DOS) partitioned into atomic l - and m -like contributions provide further details in chemical bonding.

Recently the experimental determination of the electronic charge density has been greatly improved, e.g. due to synchrotron radiation which allows to obtain structure factors with high accuracy [2]. Although the comparison between theory and experiment is made difficult by $T=0$ calculations vs. finite temperature experiments with absorption and extinction, fine details can be extracted that often agree well and lead to a better understanding of chemical bonding.

Such comparisons will be shown for a selected class of materials from oxides, SiO_2 , silicates to highly correlated systems as the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ [2] or the pyrochlore compound $\text{Y}_2\text{Nb}_2\text{O}_7$ [3]. A special feature appears in BaCoO_3 for which orbital is found to occur along the Co chains.

[1] Schwarz K., Blaha P., Madsen G.H.K., *Comp. Phys. Commun.*, 2002, **147**, 71. [2] Lippmann T., Blaha P., Andersen N.H., Poulsen H.F., Wolf T., Schneider J.R., Schwarz K., *Acta Cryst A*, 2003, **59**, 437. [3] Blaha P., Singh D.J., Schwarz K., *Phys. Rev. Lett.*, 2004, **93**, 216403.

Keywords: DFT, charge density distribution, chemical bonding

P.14.07.11

Acta Cryst. (2005). A61, C427

Electron-density Properties of the Functionally-substituted Hydroxypyrimidines

Vladimir Tsirelson^a, A. Stash^b, E. Zhurova^c, V. Zhurov^c, A. A. Pinkerton^c, V. Zavodnik^b, A. Shutalev^d, G. Gurskaya^e, A. Rykounov^f, V. Potemkin^g, ^aMendeleev University, Moscow, Russia. ^bKarpov Institute, Moscow, Russia. ^cToledo University, Toledo, USA, ^dLomonosov Academy, Moscow, Russia. ^eInstitute of Molecular Biology, Moscow, Russia. ^fChelyabinsk State University, Chelyabinsk, Russia. E-mail: tsirel@muctr.edu.ru

This work reports the results of the study of electron density and electronic energy density in the new functionally substituted hydroxypyrimidines. We performed the accurate X-ray diffraction measurements at 110 K and reconstructed the electron density and electronic energy density for three compounds of this series. *Ab initio* calculations were performed for different molecular conformations as well. In this work, we shall focus on the study of ethyl 4,6-dimethyl-2-thioxo-1,2,3,4-tetrahydroxypyrimidine-5-carboxylate. The topological analysis of the experimental and theoretical electron densities was fulfilled for all the conformations and the bonding network was quantitatively described in terms of the electron density and energy density topological features. In addition, the analysis of critical points of molecular orbitals (i.e. HOMO, LUMO) has been performed. Similar considerations were done for the other functionally substituted hydroxypyrimidines. New electron-localization/delocalization indices like the exchange energy density and correlation energy density and its Laplacians are introduced. The electron-density-based similarity of the pharmacophoric parts of the conformers of the hydroxypyrimidines studied has been estimated using new original algorithm.

This study was supported by the RFBR (grant 04-03-33053).

Keywords: electron density, accurate measurements, *ab initio* calculations

P.14.07.12

Acta Cryst. (2005). A61, C427-C428

Electron Density Study of 2,5-Dimethyl-3,4-trimethylene-6a-thiathiophthene Using XRD, XAS and DFT Calculations

Yu-Chun Chuang, Gene-Hsiang Lee, Yu Wang, *Department of Chemistry, National Taiwan University, Taipei, Taiwan.* E-mail: r92223074@ntu.edu.tw

Thiathiophthene, a planar molecule with two fused heterocyclic five-membered rings and essentially a linear S-S-S bond, is a molecule of great interest due to the unusual bonding characters and the possible aromatic properties of the two five-membered rings. In order to understand the remarkable bonding properties, the electron density distribution of one of the derivatives, i.e. 2,5-dimethyl-3,4-trimethylene-6a-thiathiophthene ($\text{C}_{10}\text{H}_{12}\text{S}_3$), was investigated both by

single crystal X-ray diffraction and by DFT calculations. The X-ray crystal structure of $C_{10}H_{12}S_3$ was studied both at 295 K and at 100 K. The Space group is $C2/m$ at 295 K, which is transformed to $P2_1/n$ at 100 K. The mirror symmetry perpendicular to 2-fold axis disappears at low temperature. Such reduction of symmetry elements was also found in a previous study on the 2,5-dimethyl-6a-thiathiophene[1]. The bond lengths of two S-S bonds are crystallographically the same [2.3341(8)Å] at 295K, but are significantly different [2.3274(5) and 2.3393(5) Å] at low temperature. The experimental electron density is produced according to multipole model. The theoretical electron density is calculated by DFT calculation, where the basis set of 6-31G** is used for all the atoms but an additional diffuse function is added for S atom. Results on the electron density distribution will be presented in terms of deformation density, Laplacian maps and the topological properties. Sulfur K-edge X-ray absorption spectroscopy (XAS) is also undertaken to further our knowledge on the electronic configuration of S atom.

[1] Wang Y., Wu S. Y., Cheng A. C., *Acta Cryst.* 1990, **B46**, 850.

Keywords: charge density, XAS, DFT calculations

P.14.07.13

Acta Cryst. (2005). **A61**, C428

An Examination of All the Inter-ion Interactions in $(CH_3)_2N(H)CH_2CH_2N(H)(CH_3)_2$ (SCN)₂

T. Stanley Cameron^a, Elinor M. Cameron^a, Joseph D. Ferrara^b, T. N. Guru Row^c, Parthapratim Munshi^c, ^aDalhousie University, Halifax, Canada. ^bRigaku MSC, The Woodlands, Texas. ^cSolid State and Structural Chemistry, IISc, Bangalore, India. E-mail: Cameron@Dal.Ca

N,N,N',N' -tetramethylethylenediammonium $(CH_3)_2N(H)CH_2CH_2N(H)(CH_3)_2^+$ forms a di-thiocyanate hydrogen bonded salt in space group $P-1$ with $Z = 1$. X-ray data were collected on a Saturn 70 with Mo- K_α radiation to $2\theta(\max) = 105^\circ$. The multipole refinement was performed via XD [1] and all the topological interactions were then investigated. Of the 8 unique C-H hydrogen atoms, all but one forms significant interactions to the thiocyanate anion. These interactions constitute 4 (C-H...S), 2(C-H...C), 2(C-H... $\pi(C\equiv N)$), and 2(C-H...N) with two bifurcated C-H interactions. All 10 interactions satisfy all the eight of Koch & Popelier's criteria [2] for a weak interaction, though one interaction of a bifurcated pair is only marginally satisfactory. The N-H...N classical hydrogen bond is found to have weakened in the crystal when compared with the theoretically calculated values for an isolated ion pair.

[1] Koritsanszky T. S., Howard S., Macchi P., Gatti, C., Farrugia L. J., Mallinson P. R., Volkov A., Su Z., Richter T., Hansen N. K., *XD (version 4.10, July): A computer program package for multipole refinement and analysis of electron densities from diffraction data*, 2003. [2] a) Koch U., Popelier P. L. A., *J. Phys. Chem.* 1995, **99**, 9747; b) Popelier P., *Atoms in Molecules*, Prentice Hall, UK, 2000, 151.

Keywords: multipole refinement, hydrogen bonding, topological properties of charge distribution

P.14.07.14

Acta Cryst. (2005). **A61**, C428

Rb_4C_{60} Equation of States and Electronic Density Study by Compton Scattering

Geneviève Loupias^a, Amir Sabouri-Dodaran^a, Christophe Bellin^a, Massimiliano Marangolo^a, Francesco Mauri^a, Sohrab Rabbii^b, Mohamed Mezouar^c, Thomas Buslaps^c, ^aIMPMC, University of Paris 6, France. ^bUniversity of Pennsylvania Philadelphia, U.S.A. ^cESRF, Grenoble, France. E-mail: loupias@lmcp.jussieu.fr

In the family of compounds A_nC_{60} ($A=K, Rb$ and Cs ; $n=1,3,4$ and 6), Rb_4C_{60} exhibits an unusual behavior: it is a non-magnetic insulator at ambient pressure, whereas expected as a conductor, even a superconductor (cf. Rb_3C_{60}), by theory [1]. Furthermore Rb_4C_{60} undergo an insulator to metal transition under pressure around 0.8 GPa, as observed by NMR study of Rb_4C_{60} [2].

We have performed combined Compton scattering (ID15B) and diffraction experiments at ESRF (ID-30), at pressures below and

above the insulator-metal transition. Our diffraction experiment exhibits, for the first time, an abrupt jump in compressibility between 0.5 GPa and 0.8 GPa. We attributed this jump to a structural phase transition preserving the initial tetragonal symmetry [3]. By *ab-initio* calculations we reproduced the experimental phase transition and studied the pressure dependence of internal coordinates. Going further, the comparison with *ab-initio* LDA calculations allowed us to quantitatively evaluate contributions due to contraction of the unit cell as well as an unexpected contraction of the C_{60} molecule itself, evidenced by Compton measurements. In fact, this C_{60} molecule contraction leads to a major effect on electronic density of Rb_4C_{60} compound [5].

[1] Erwin S.C., *Buckminsterfullerenes*, ed. W. E. Billups M. A. Ciufolini, VCH, New York, 1993, 217. [2] Kerkoud R. *et al.*, *J. Phys. Solids*, 1996, **57**, 143. [3] Sabouri-Dodaran A.A. *et al.*, *Phys. Rev.*, 2004, **B70**, 174114.

Keywords: structural change, Compton scattering, high-pressure X-ray diffraction

P.14.07.15

Acta Cryst. (2005). **A61**, C428

An Examination of All the Inter-ion Interactions in Tetraphenylphosphonium Squarate

David Wolstenholme^a, T. Stanley Cameron^a, Joseph D. Ferrara^b, Katherine N Robertson^a, ^aDalhousie University, Halifax, Canada. ^bRigaku MSC, The Woodlands, Texas. E-mail: dwolsten@dal.ca.

The tetraphenylphosphonium squarate salt crystallises with a hydrogen bonded dimeric squarate anion in space group $P2_1/n$ with $Z = 4$. X-ray data were collected on a Saturn 70 with Mo- K_α radiation to $2\theta(\max) = 76^\circ$ at $-153^\circ C$. The multipole refinement was performed with XD [1] and all the topological interactions were then investigated. Currently of the 20 unique C-H hydrogen atoms, all but two form significant interactions either to the squarate ion (C-H...O interactions) or among the phenyl groups C-H...H-C, or C-H... π (Ph). The two remaining 'non-interacting' (C)H atoms are adjacent *ortho* hydrogen atoms, that look as though there ought to be an intramolecular H...H interaction though this has not yet been fully characterized. The remaining interactions satisfy all the eight of Koch & Popelier's criteria [2] for a weak interaction. The O-H...O classical hydrogen bond of the squarate is found to have weakened in the crystal when compared with the theoretically calculated values for an isolated dimeric anion

[1] Koritsanszky T. S., Howard S., Macchi P., Gatti, C., Farrugia L.J., Mallinson P.R., Volkov A., Su Z., Richter T., Hansen N. K., *XD (version 4.10, July): A computer program package for multipole refinement and analysis of electron densities from diffraction data*, 2003. [2] a) Koch U., Popelier P. L. A., *J. Phys. Chem.*, 1995, **99**, 9747; b) Popelier, P., *Atoms in Molecules*, Prentice Hall, UK, 2000, 151.

Keywords: multipole refinement, hydrogen bonding, topological properties of charge distribution

P.14.07.16

Acta Cryst. (2005). **A61**, C428-C429

X-ray Charge Density of a New Magnetic Metal Organic Framework, $Mn_3(C_8O_4H_4)_3(C_5H_{11}ON)_2$

Rasmus Damgaard Poulsen, Anders Bontien, Marie Chevalier, Bo B. Iversen, *Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus, Denmark*, E-mail: rdp@chem.au.dk

A new magnetic metal organic framework material has been synthesized, $Mn_3(C_8O_4H_4)_3(C_5H_{11}ON)_2$.¹ Magnetic susceptibility measurements from 2 to 400 K reveal anti-ferromagnetic ordering at ~4 K and a total magnetic moment of 6.0 μ_B . The magnetic phase transition is confirmed by heat capacity data (2 - 300 K). The crystal structure is studied by conventional single crystal X-ray diffraction data at 300, 275, 250, 225, 200, 175, 150, 125 and 100 K, and synchrotron data at 20 K. The electron distributions around the two unique Mn centers are different, and both have substantial anisotropy. Orbital population analysis reveals large electron donation (1.7 e) to each Mn atom and the maximum possible number of un-paired electrons is 3.2 for both