

P14.07.13*Acta Cryst.* (2008). A64, C569**Charge density of Ni(MePh)₂(C₆F₅)₂ (1) and the energy density in the Ni-C bond**Christophe M. L. Vande Velde¹, Philip Coppens²¹Universite Libre de Bruxelles, Chimie des Polymeres, CP206/1, Brussels, Brussels, B-1050, Belgium, ²State University of New York at Buffalo, Dept. of Chemistry, 737 NSC, Buffalo, NY-14260-3000, USA, E-mail : christophe.vande.velde@ulb.ac.be

(1) was synthesised as a model compound for conducting metal-organic oligomers and polymers, and a charge density study was conducted in order to gain insight into the sigma carbon-nickel bond, which is often formally represented as Ni²⁺-C. The results presented here, in combination with theoretically obtained values, demonstrate that the character of the Ni-C bond is far from ionic, and various parameters are presented that provide a much more nuanced image of this type of carbon-metal sigma bonding. Charges are calculated and compared with literature values, indicating that the nickel atom in this kind of compound is the most electron-rich nickel atoms known. The energy density is evaluated as a criterion for bond characterisation in this complex.

Keywords: charge density studies, metal organic compound, nickel compounds

P14.07.14*Acta Cryst.* (2008). A64, C569**Experimental and theoretical charge density study of a compound containing linear tri-selenium bond**Yu-Chun Chuang¹, Chou-Fu Shou¹, Yi-Hung Liu², Gene-Hsiang Lee², Yu Wang¹¹National Taiwan University, Department of Chemistry, No. 1, Sec. 4, Roosevelt Road, Taipei, none, 10617, Taiwan, ²Instrumentation Center, National Taiwan University, Taipei, 10617, Taiwan, E-mail : d94223006@ntu.edu.tw

The compound, 3,4-trimethylene-6a-selenaselenophthene, is a planar molecule with two fused heterocyclic five-membered rings and a linear Se-Se-Se part. The electron density distribution is aimed at the understanding of the aromatic properties of the two five-membered rings and the rather unusual bond characters of Se-Se-Se bond. The electron density distribution will be derived both from accurate diffraction data experimentally and from the molecular orbital calculations theoretically. The experimental data were measured at 100K twice: one with wavelength of 0.5Å on a synchrotron source (SPring8 BL12B2); the other with Mo Kα on a in house CCD diffractometer. The deep violet rod crystal is rather small in two dimensions ~ 30μ, it crystallized in orthorhombic space group *Pna*2₁ with unit cell dimension 11.2388(2), 16.4710(3) and 4.8867(1) Å. Two Se-Se bonds are 2.5486(5) and 2.5617(5)Å respectively. Detail comparison between two sets of data will be presented. Bond characterization will be given in terms of deformation density and the topological analysis. The corresponding theoretically calculated density is also going to be displayed. The topological properties associated with the chemical bond will be listed in comparison with the experimentally derived ones.

Keywords: charge density, selenium-selenium bond, synchrotron diffraction

P14.07.15*Acta Cryst.* (2008). A64, C569**Population of atomic orbitals in silicide vanadium**Boris N Kodess, Svetlana R Sambueva, Ismail F Massalimov
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Based on a precision experiment carried out at room temperature (MoK-alpha, full sphere to sin teta/lambda 1.3) difference maps of electron density distribution in V3Si are draw. The achieved accuracy allows to calculate charge distribution numerical characteristics. A refining commonly used the overdetermined least-squares method can lead to rather deep but only local minimum values unless a multi-step selection and accounting of a large number of factors are made. This local minimum [s a results of corrections which may affect in different ways on the quality of a structural model. Therefore, the importance of our procedure is consecutive refinement of the structural model (to a level of R-values of around 1 per cent), initially without using a multipole model. This means that the introduction of several additional multipole parameters at the earlier achieved accuracy levels can lead to false R-factors reduction simply by increasing the number refined parameters. The required level has been achieved due to choosing a better strategy and by optimizing tactics of carrying out the experiment, data processing, and refinement of structural parameters especially. The calculation of atomic orbitals population made based on the experimental data and compared with theoretical calculation of the "first principles" done by B. Matheis (after expansion of his calculated electronic distribution in the same basis of atomic orbitals). The shown results speak of a good quality of the experiment and processing of the received data, as well as about the correct choice of a model made by B. Matheis. It should be noted that the results of other semi-phenomenological calculations show a significant difference in value as well, and sometimes in the transferred charge sign.

Keywords: higher accuracy, charge density distribution, atomic orbitals population

P14.07.16*Acta Cryst.* (2008). A64, C569-570**Structural phase transitions in Rb₂Mn₂(SO₄)₃: A charge density study**

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The langbeinite family of sulfates with the general formula A₂B₂(SO₄)₃ with A = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, (NH₄)⁺ and B = Mg⁺², Mn⁺², Ni⁺², Ca⁺² represents a class of ferroelastic and ferroelectric materials (1). X-ray diffraction studies have shown that crystals of these materials have a cubic structure with space group *P*2₁3 at room temperature with a lattice parameter of nearly 10 Å and four formula units per unit cell. Theoretical calculations by Dvorak (2) suggest that these crystals can transform to low temperature phases with several possible space groups *P*2₁, *R*3, *P*1 and *P*2₁2₁2₁. So far in the literature there have been two different sequences of phase transition identified (3), one with cubic to orthorhombic distortion and the other with cubic - monoclinic - triclinic - orthorhombic distortion. Very high quality crystals of Rb₂Mn₂(SO₄)₃ were grown from slow evaporation of equimolar aqueous solution of the respective salts [Rb₂SO₄:2MnSO₄]. The charge density data sets for this material

at 200K (Cubic, $P2_13$) and at 100K (Orthorhombic, $P2_12_12_1$) respectively were collected and analyzed by using XD2006 package (4). The topological analysis and calculation of relevant properties bring out the salient features which allow for a clear distinction in bond paths, Laplacian maps and electrostatic potential isosurfaces in both metal coordination and sulfate tetrahedra across the phase transition.

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Keywords: charge density, mineral structures, sulfates

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Tartaric acid gyration tensor components from charge density distribution

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L-tartaric, (+)-(2R,3R)-2,3-dihydroxybutanedioic, acid crystallizes in non-centrosymmetric space group $P2_1$. Experimentally determined principal components of the gyration tensor [1] and the optical rotation calculated from the structural data using Pauling's atom volume polarizabilities [2] differed significantly. Since the contribution of the molecule itself to optical activity of the crystal was estimated as relatively small, the predominating intermolecular effects were expected to be responsible for the high gyration tensor components. To get necessary information, charge density analysis was performed [3] using the program package XD [4] and low-temperature (80 K) X-ray diffraction data. The results of the topological analysis of $\rho(r)$ at the bond critical points gave a quantitative description of the hydrogen bonds whereas the properties of charge density distribution enabled the derivation of atom volume polarizabilities [5,6] which in turn were utilized for the determination of gyration tensor components. This work is partially supported by the Polish Ministry of Education and Science (grant No. N204 124 32/3169).

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Keywords: charge density distribution, optical rotation, atom volume polarizability

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Chemical bonding in energetic RDX: An experimental and theoretical study

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Accurate X-ray diffraction data at 20K and 120K were obtained for the alpha-form of the 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX) crystal using a Rigaku R-Axis Rapid high-power rotating anode diffractometer with a curved image plate detector. Data were integrated with the program VIIPP [1] using the predicted reflection positions from the program HKL2000 [2], scaled and averaged with SORTAV [3], and the multipole refinements performed with the XD program package [4]. The experimental electron density (ED) obtained at two temperatures has been analyzed in terms of the Quantum Theory of Atoms in Molecules, and compared with the ED calculated theoretically. Features of the intra- and inter-molecular bond critical points and the oxygen atom lone-pair locations are discussed. Hydrogen bonding, O · · · O, O · · · N and N · · · N intermolecular interactions are reported. Atomic charges, features of the electrostatic potential and the molecular dipole moment are discussed.

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Keywords: experimental charge density, topological analysis, Image plate

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Application of the aspherical scattering formalism on the refinement of macromolecules

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The conventional modelling of an X-ray diffraction experiment makes use of the "Independent Atom Model (IAM)", which ignores a priori electron density asphericities caused by the interaction of atoms. The Hansen&Coppens multipole model allows for a non-spherical atomic description but may require more than 40 parameters per atom and therefore needs high resolution diffraction data ($d < 0.5 \text{ \AA}$), which is mostly far beyond the scattering power of macromolecules. The recently introduced invariom model overcomes this limitation by assignment of individual aspherical scattering factors (multipoles) to each chemically unique atom in a structure. This permits to refine only atomic positional and vibrational parameters and thus to use data sets of medium resolution ($d < 0.9 \text{ \AA}$). The invariom library covers all bonding situations in polypeptides. Numerous tests on small molecules showed that this approach improves the accuracy of the molecular geometry, yields a better description of the displacement parameters and more accurate Flack parameters even in the case of limited resolution. But so far