

The functions can be compared with experimental ones, obtained by refinements in small ranges of  $S$ , taking the positions from very high angle refinements as a reference. Calculated and experimental values are in excellent agreement.

Shifts observed can be rationalized in terms of competition of bonding and lone pair difference densities: the bonding densities dominating at low  $S$ , the lone pair densities at high  $S$ .

**PS09.02.11 ON THE RELATION BETWEEN FREQUENCY SHIFTS AND ELECTRON DENSITY SHIFTS.** Kersti Hermansson, Dept. of Chemistry, Uppsala University, Box 531, S-75121 Uppsala, Sweden

The frequency shift of the intramolecular stretching vibration of a diatomic molecule is a sensitive probe of the strength and nature of intermolecular bonding. For some diatomics, the intramolecular bond gets stronger, for others weaker, when the molecule is bound by intermolecular forces.

The poster explains how electron density maps of the vibrating free molecule will tell us if a frequency upshift or a downshift will occur when the molecule is bound in a crystal.

**PS09.02.12 ELECTRON DENSITY DISTRIBUTION ON TWO IMINO COMPLEXES,  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2]^{2+}[\text{ClO}_4]_2^-$  AND  $[\text{Cu}(\text{N}_2\text{O}_2\text{C}_{16}\text{H}_{14})]_2$ .** J. J. Lee, C. H. Hwang, G. H. Lee, Yu Wang\*, Y. S. You, S. M. Peng, Department of Chemistry, National Taiwan University, Taipei, Taiwan

The crystal and molecular structures of  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2]^{2+}[\text{ClO}_4]_2^-$  and  $[\text{Cu}(\text{N}_2\text{O}_2\text{C}_{16}\text{H}_{14})]_2$  have been determined by single-crystal X-ray diffraction method at 295 and 125 K. The former crystallizes in the space group of  $Pbca$  at 125 K with cell parameters  $a=11.655(2)$ ,  $b=16.930(4)$ ,  $c=10.508(2)\text{\AA}$ ,  $M_w=556.27$ ,  $V=2073.4(6)\text{\AA}^3$ ,  $Z=4$ . The molecular symmetry is  $C_1$  with the Co atom at the 1 position; the latter one crystallizes in the space group  $C2/c$  with cell parameters  $a=26.609(2)$ ,  $b=6.9143(4)$ ,  $c=14.567(2)\text{\AA}$ ,  $M_w=559.68$ ,  $V=2073.4(6)\text{\AA}^3$ ,  $Z=4$ . The molecule is a dinuclear complex with molecular symmetry of  $C_1$ .

In the Co complex, the Co atom is coordinated by four imino N at the macrocyclic plane and two water molecules at the axial position. The Co-N distances are  $1.9026(7)\text{\AA}$  and  $1.9153(7)\text{\AA}$ . The  $\text{CoN}_4\text{O}_2$  can be described as a tetragonal distorted octahedron due to Jahn - Teller distortion. The ligand is a partially  $\pi$ -delocalized  $\alpha$ -diimine ligand, the C-N bond distance is  $1.301(1)\text{\AA}$ , indicating a double bond character, and the N-N bond is  $1.373(1)$  and  $1.382(1)\text{\AA}$ , which is a single bond character. In the Cu complex, the Cu ion is five coordinated ( $\text{N}_2\text{O}_5$ ) with one oxygen atom served as bridge between two Cu ions. The Cu-N distances are  $1.9567(8)$  and  $1.9596(8)\text{\AA}$ . Electron density distribution based on multipole refinement confirms the prediction on the asphericity in electron density around the metals. The bonding between imino nitrogen and metal ions (Co and Cu) can be recognized as a  $\sigma$ -donor from N, the density depletion is found along the  $d_\sigma$  direction on both complexes. Electron density distribution on low spin  $d^7$  Co(II) and  $d^9$  Cu(II) will be displayed. Detail comparison between experimental and theoretical results will be presented for Co-complex. Strong covalent bond characters are found on ligand part in both complexes.

**PS09.02.13 COMPARING 90K DATA TO SOLID STATE AB-INITIO CALCULATIONS FROM CRYSTAL92** Anthony Martin, Dept of Chemistry, University of Toledo, Toledo, OH 43606, USA. A. Alan Pinkerton, Dept of Chemistry, University of Toledo, Toledo, OH 43606, USA, A. Barry Kunz, Dept of Electrical Engineering, Michigan Technological University, Houghton, MI 49931, USA.

Accurate X-ray diffraction measurements on Ammonium Dinitramide, Biguanidinium Dinitramide and bis-Biguanidinium Dinitramide have been made at 90K. The resulting multipole refinements are compared to the calculated charge densities at the 6-21G basis set level using CRYSTAL92 for each system. The solid state ab-initio calculations use the 90K unit cell and geometries. The N-H bonds are all fixed at idealised neutron positions. Thus, there is no geometry optimization in the ab-initio calculation. The ab-initio calculations are all at 0K and do not include any zero-point energy. Thermal motion has been taken into account by either setting the multipole thermal parameters to zero before calculating charge densities from the x-ray data or thermally smearing the ab-initio data with the experimental thermal parameters.

Preliminary work indicates that there are significant differences in the position of the bonds and lone pair peaks when the two methods are compared.

**PS09.02.14 A DATABASE AND MOLECULAR ORBITAL STUDY OF INTRAMOLECULAR STRONG HYDROGEN BONDS IN METAL-DIGLYOXIME SYSTEMS.** Kevin W. McConnell and Ronald F. See, Department of Chemistry, Saint Louis University, St. Louis, MO 63103

The nature of strong hydrogen bonds has long been of interest, both as a test to theories of chemical bonding and, more recently, as a key step in the hydrogen transfer mechanism of certain enzymatic catalysis. For O-H...O systems, strong hydrogen bonds may be defined as those with a distance of less than  $2.8\text{\AA}$  between the oxygen atoms. Metal-diglyoxime complexes provide an excellent opportunity to compare strong hydrogen bonds, as changes in both steric and electronic effects are quantifiable. A search of the Cambridge Structure Database has resulted in approximately 150 known metal-diglyoxime structures, each containing two strong intramolecular hydrogen bonds, ranging from  $2.40$  to  $2.80\text{\AA}$  between oxygen atoms. Results of this search suggest that electron-withdrawing substituents on the glyoxime backbone favor stronger intramolecular hydrogen bonds; a possible explanation for this trend will also be presented. In order to test theoretical predictions against experimental results, molecular orbital calculations (ZINDO) were performed on nickel diglyoxime model compounds containing the substituents  $-\text{CH}_3$ ,  $-\text{NH}_2$ ,  $-\text{OH}$  and  $-\text{F}$ . The results of these calculations are not totally consistent with the empirical trends identified through the database search. These results will be analyzed in terms of Brown's bond-valence theory, as well as Gilli's resonance-assisted hydrogen bonding concepts.

**PS09.02.15 DENSITY FUNCTIONAL STUDY OF AMMONIUM FLUORIDE: A COMPARISON BETWEEN THEORY AND EXPERIMENT** Hans Overeem, Roelof Y. de Vries and Dick Feil, Chem. Phys. Lab. University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.

In the molecular ion of  $\text{NH}_4^+$  a large part of the electrons is involved in bonding. The electron density distribution is strongly influenced by the electric field of the F<sup>-</sup> ions.

The present study deals with quantum chemical density functional calculations on the crystal of  $\text{NH}_4\text{F}$ . In molecular crystals, cluster calculations have been successful (Krijn et al, 1988). For

ionic crystals, the cluster method meets serious problems: What is the potential? How to account for periodicity?

The present calculations were performed using Bloch functions to account for periodicity and a potential calculated with the Ewald method (program ADF-BAND (te Velde et al, 1990)). Dynamic structure factors were calculated and compared with multipole refined low-temperature data (van Beek et al, 1996). The difference amounted to  $R(F)=1.6\%$ .

Realizing that multipole refinement not only reduces noise, but also introduces bias, the theoretical data were refined with the same POP-multipole program. This reduced the difference with experiment to  $R(F)=0.8\%$ , the remainder for the greater part due to the  $\text{NH}_4$  group ( $R(F)=1.1\%$ ) and to a lesser part to the fluorine. Electron density maps corresponding with the various differences will be shown.

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C.G.van Beek, J.Overeem, J.R.Ruble and B.M.Craven, (1996) *Canadian Journal of Chemistry*, (accepted for publication).  
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**PS09.02.16 TOPOLOGICAL PROPERTIES OF ELECTRON DENSITY OF PENTAFLUOROSULFANYL DERIVATIVES.** G. J. Perpetuo, T. Koritsanszky, D. Preugschat, D. Lentz and P. Luger, Institute for Crystallography and Institute for Inorganic Chemistry Free University of Berlin, Germany

Topological analyses of experimental and theoretical electron densities and Laplacian functions of the title compounds ( $\text{SF}_5\text{X}$ ,  $\text{X} = \text{NC}$ ,  $\text{NCO}$  and  $\text{CN}$ ) are presented. The parameters of a static density model based on the multipole formalism /1,2/ has been extracted from high-resolution X-ray diffraction data collected at 120 K. Ab-initio calculations /3/ have also been performed at the Hartree-Fock and MP2 level of theory utilizing 6-311G+(3df) and 6-311G\* basis sets, respectively. Geometry optimizations were also carried out. In the case of  $\text{SF}_5\text{NCO}$  the asymmetric unit consists of two conformers; the isocyanate being in eclipsed and straggled position with respect to the equatorial  $\text{SF}_4$  moiety. Calculations at the MP2 level show the latter to correspond to a transitional state. The experimental bond-topological properties /4/ (the electron density and its Laplacian at the bond critical points) occur to be overestimated compared to those calculated from wavefunctions. The application of high basis sets including polarization and diffuse functions is proved to be important. The degree of the covalent character of the S-F bonds in the different molecules is compared.

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/2/ T. Koritsanszky, S. Howard, P.R. Mallinson, Z. Su, T. Richter and N.K. Hansen: XD a Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data, 1995.

/3/ Gaussian 92/DFT, Revision G.4, J. A. Pople et al, Gaussian, Inc., Pittsburgh PA, 1993.

/4/ R.F.W. Bader, *Atoms in Molecules: A Quantum Theory*; Clarendon Press, Oxford, U.K., 1990.

**PS09.02.17 THEORETICAL AND EXPERIMENTAL ELECTRON DENSITY ANALYSES OF DIHYDROXY BENZOPHENONE.** F. K. Ross, Z. Hu, and R. Glaser, Research Reactor Center and Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA

Detailed electron density distributions for dihydroxybenzophenone (DHBP,  $\text{C}_{13}\text{H}_{10}\text{O}$ ) have been obtained from X-ray+Neutron (X+N) diffraction analysis and by ab initio molecular orbital calculations(1) for a closely analogous structure. Various mechanisms for accounting for H atom bond polarization in the X+N model are tested and compared with results from theory. Anharmonic thermal motion appears to be a significant effect and must be adequately modeled before good agreement of the two

methods is achieved. Comparisons of charge density distributions, orbital population parameters, potential maps and critical points will be discussed.

(1) R. Dovesi, V.R. Saunders and C. Roetti, CRYSTAL92, An ab-initio Hartree-Fock LCAO program for periodic systems, University of Turin and SERC, Daresbury (UK).

**PS09.02.18 THE CRYSTAL STRUCTURE OF PALLADIUM DIPHENYLGlyoxime; AN ANALYSIS OF STRONG HYDROGEN BONDS IN PALLADIUM-DIGlyoxime COMPOUNDS.** Ronald F. See, Christopher Curtis and William M. Strub, Department of Chemistry, Saint Louis University, St. Louis, MO 63103, Joseph W. Ziller, Department of Chemistry, University of California at Irvine, Irvine CA 92717

When the 2+ ions of group 10 metals, such as palladium, react with bidentate glyoxime-type ligands, the result is a four-coordinate, square-planar compound where the glyoxime moieties are linked by intramolecular strong hydrogen bonds of the O-H-O type. The nature of these strong hydrogen bonds has long been of interest, in as much as they offer a serious challenge to theories of chemical bonding. Palladium(II)-diglyoxime complexes provide an excellent opportunity to compare strong hydrogen bonds, as changes in the hydrogen bonds can be measured against the electronic effects of the substituent groups on the glyoxime backbone. The structure of the title compound,  $\text{Pd}(\text{dpgH})_2$  (dpg = diphenylglyoxime), was refined to  $R = 4.46\%$  for  $4\sigma$  data and  $7.90\%$  for all data. The distance between the oxygen atoms involved in the intramolecular hydrogen bond is  $2.550(10)$  Å. There is strong evidence that the hydrogen atom involved in this hydrogen bond is in a nearly-centered (though asymmetric) position. This structure can be compared with those previously reported structures of palladium-diglyoxime compounds, which have the substituents -H, - $\text{NH}_2$ , - $\text{CH}_3$  and  $\alpha$ -furyl. Use of the Hammett parameters allows one to quantify the electronic effects of the substituent groups, and thus to investigate the response of the intramolecular hydrogen bond to changing electronic environments. These results indicate that electron-withdrawing groups tend to strengthen the hydrogen bond; it may be possible to explain this observation with reference to bond valence theory.

**PS09.02.19 CHARGE DENSITY DISTRIBUTION IN  $\text{AgGaS}_2$ .** Roland Spengler, Andreas Bram, Hans Burzlaff, Institut für Angewandte Physik, Lehrstuhl für Kristallographie, Universität Erlangen-Nürnberg, Bismarckstraße 10, 91054 Erlangen, Germany, Volker Krämer, Kristallographisches Institut, Universität Freiburg, Hebelstr. 25, 79104 Freiburg/Br., Germany.

$\text{AgGaS}_2$  is one of the most interesting materials for applications as photovoltaic semiconductor in sandwich photo cells because of its large band gap. Jaffe & Zunger [1,2] explained the energy gap by a strong contribution from the d-orbitals of the Ag-atoms following their pseudo-potential calculations.

Experimental measurements at 293K, 105K and 25K on a self-constructed 4-circle diffractometer using HUBER mechanics, an APD-cryostat and self-developed interfaces and software [3] show an increasing order of the non-spheric charge density at Ag and Ga with decreasing temperature [4]. It was possible to obtain information about the occupancy of the  $d_{z^2}$ ,  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ -orbitals.

These observations are in agreement with charge density calculations made by A. Shaukat et.al. [5]. Quantitative parameterization of the occupancy of the d-orbitals and a comparison of theory and experiment shall be presented.

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