

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