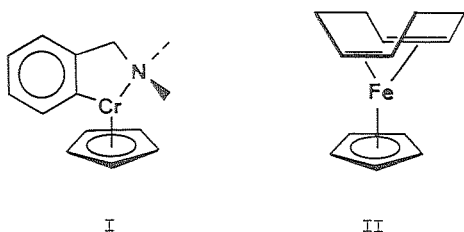


06.2-31 EXPERIMENTAL CHARGE DENSITY STUDY OF  $(\text{CH}_2\text{SO}_2)_2$ . By Y. Wang, C.T. Kao, C.J. Tsai, L.W. Guo; Dept. of Chem., National Taiwan University. J.W. Bats, Univ. of Frankfurt.

Single crystal of 1,3-dithietane-1,1,3,3-tetraoxide was studied by x-ray diffraction at  $300^\circ\text{K}$  and  $104^\circ\text{K}$ . It crystallized in monoclinic  $P 2_1/n$ .  $a=5.527(2)$ ,  $b=5.709(1)$ ,  $c=8.042(2)\text{\AA}$ ,  $\beta=100.89(3)^\circ$  and  $Z=2$ . The crystals are a four membered S-C-S-C ring with the center of the ring at  $\bar{1}$ . Using all the observed reflections below  $\sin\theta/\lambda$   $0.66\text{\AA}^{-1}$ , the structure was refined to  $R=0.020$ . Distances and angles are : S-C  $1.8058(8)$ ,  $1.8096(6)\text{\AA}$ ; S-O  $1.4353(5)$ ,  $1.4376(6)\text{\AA}$ ; C-S-C  $88.37(3)^\circ$ ; O-S-O  $118.84(3)^\circ$ . A charge density study was performed on  $104^\circ\text{K}$  data. The X-X deformation map of the 4-membered ring showed significant amount of density around sulfur atom but nothing significant between the two sulfur atoms (non-bonding distance  $2.593\text{\AA}$ ). There is  $0.57\text{ e/\AA}^3$  in the S-C bond but polarized toward sulfur atom.  $\text{SO}_2$  plane is perpendicular to the 4-membered ring ( $88.6^\circ$ ). The density of S-O bond is at the center of the bond.

06.2-32 AB INITIO THEORETICAL CALCULATIONS OF THE ELECTRON DEFORMATION DENSITY FOR BENZYLAMINECYCLOPENTADIENYLCHROMIUM AND CYCLOOCTADIENECYCLOPENTADIENYLIRON. A COMPARISON OF THEORY WITH EXPERIMENT. By R. Goddard, MPI für Kohlenforschung, D-4330 Mülheim-Ruhr, FRG.

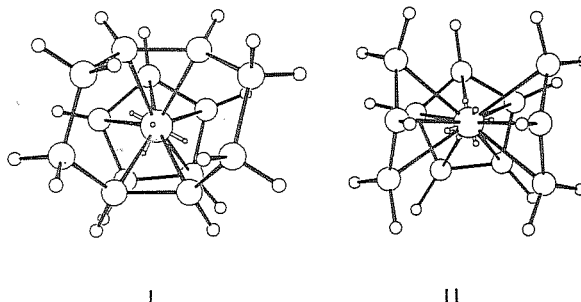
This paper describes the results of the calculation of the static electron deformation density distribution for  $\text{C}_5\text{H}_5\text{Cr}(\text{C}_{12}\text{H}_{13}\text{N})$ , I, and  $\text{C}_5\text{H}_5\text{Fe}(\text{C}_8\text{H}_{13})$ , II, by *ab initio* methods at the double- $\zeta$  level (AIMOL, V.R. Saunders 1976). The deformation densities are compared with each other and with those determined by experiment, (X-X) (X-N).



The distribution of the charge around the metals is discussed in terms of the electron count on the metal (the oxidation state), the nature of the ligands and their geometrical arrangement. An explanation for the stability of these unsaturated complexes (I,  $14e^-$ ; II,  $17e^-$ ) is suggested. A general approach for predicting the positions of the maxima about a transition metal based on simple ligand field theory is proposed and developed for more complicated systems.

06.2-33 THE ELECTRON DENSITY DISTRIBUTION IN TWO ISO-ELECTRONIC CYCLOPENTADIENYL-TRANSITION-METAL COMPLEXES. By C. Krüger, R. Goddard, and J. Allibon\*, MPI für Kohlenforschung, D-4330 Mülheim-Ruhr, FRG and \*Institut Laue-Langevin, F-38042-Grenoble, France.

The deformation density distribution (X-X, and X-N for I,  $100\text{ K}$ ) in the two isoelectronic, paramagnetic  $17e^-$ -transition metal complexes,  $\text{C}_5\text{H}_5\text{Fe}(\text{C}_8\text{H}_{12})$  (I) and  $\text{C}_5\text{H}_5\text{Mo}(\text{C}_3\text{H}_5)_2$  (II), are compared.



Both compounds show an octahedral electron density distribution about the metal. The orientation of the octahedra with respect to the ligands is similar in the two complexes, but there are significant differences (see figures).

The spacial arrangement of the electron density around the metals appears to have stereochemical consequences and provides an explanation for the observed chemical behaviour of these and similar compounds.

06.2-34 A CHARGE DENSITY STUDY OF THE CUBIC FORM OF BORON NITRIDE. By B. Josten, A. Kirfel and G. Will, Mineralogisches Institut der Universität Bonn, Lehrstuhl für Mineralogie und Kristallographie, Poppelsdorfer Schloß, D-5300 Bonn, FRG.

$1253(\text{MoK}\alpha)$  and  $3013(\text{AgK}\alpha)$  measurements of the X-ray structure amplitudes of the cubic BN ( $a = 3.6153(2)\text{\AA}$ ;  $F\bar{4}3m$ ) were carried out up to a maximum  $2\theta = 156^\circ$ , resulting in sets I and II of 41 and 76 observed unique reflections respectively. The conventional refinements of the spherical-atom model yielded agreement factors  $R = 0.0156$ ,  $R_w = 0.0202$  (set I) and  $R = 0.0203$ ,  $R_w = 0.0239$  (set II). The isotropic temperature factors of B and N and the respective scale factors were determined from high-order refinements and used for ensuing calculations of  $X-X^{\text{HO}}$  difference density-, valence density- and deformation potential distributions in the (110) and (111) planes.

Further studies of the charge density distribution in BN were based on two models, both leading to significantly improved least-squares fits to the data: a) the "bond model" with a

point scatterer initially placed on the middle of the B-N bond ( $R = 0.0070$ ,  $R_w = 0.0105$  (set I) and  $R = 0.0105$ ,  $R_w = 0.0153$  (set II)), and b) the multipole model (Hirshfeld, Israel J. Chem. (1977) 16, 226) including atomic monopole-, octopole- and hexadecapole scattering functions ( $R = 0.0050$ ,  $R_w = 0.0088$  (set I) and presently  $R = 0.0127$ ,  $R_w = 0.0160$  (set II)). The refined multipole parameters served to calculate sections of the static deformation density distribution.

All results show that the B-N bond contains a considerable ionic contribution in agreement with the respective electronegativities of 2.0 (boron) and 3.0 (nitrogen).

06.2-35 RE-DETERMINATION OF THE CHARGE DENSITY DISTRIBUTION IN BERYLLIUM METAL. By V.G. Tsirel'son, N.N. Lobanov, R.P. Ozerov, Mendeleev Institute of Chemical Technology, Moscow, USSR.

The experimental deformation electron density distribution (DEDD) in beryllium metal was studied by the modern treatment of Brown, X-ray diffraction data with extinction-free (1010), (0002) and (1011) reflections measured by Suortti and the neutron thermal parameters. Maps of DEDD in (00z) planes with  $z = 0, 0.125, 0.250$  were calculated. Positive peaks of "covalent" electron density (0.016 a.u.) have been found in interatomic space. Positive peaks (0.098 a.u.) have been observed on Be atoms positions. This indicates that Be atoms in the metal are contracted in comparison with free state. As it has been established earlier in diamond, V, Cr, etc. excess of electronic part of electrostatic potential at Be position was found on potential distribution maps. Accordingly to the Politzer functional density approach these features correspond to the bonded state of Be atoms in metal.

06.2-36 X-RAY DIFFRACTION STUDIES OF THE CHARGE DENSITY IN PORPHYRINS: MESOTETRAPHENYL PORPHINATO BIS (TETRAHYDROFURAN) IRON II. By C. Lecomte<sup>a</sup>, P. Coppens<sup>b</sup>, R.H. Blessing<sup>c</sup>, and Liang Li<sup>d</sup>. a) Laboratoire Cristallographie ERA162 54506 VANDOEUVRE LES NANCY FRANCE. b) Chemistry Department STATE UNIVERSITY OF New York, BUFFALO, N.Y. 14214 USA. c) Medical foundation of Buffalo, 73 High street, BUFFALO, N.Y. 14203 USA.

The crystal structure and experimental electron density distribution of (meso-tetraphenyl porphinate) bis (tetrahydrofuran) iron II has been determined from high resolution single crystal X-ray diffraction measurements at 120K. This complex contains a six coordinate iron II atom which has an unusual high spin electronic ground state.

The detailed analysis was based on 7300 unique independent reflections by averaging of 11610 and 9490 reflections respectively measured at 120K on two different crystals. Both data sets were scaled ( $R_w(F^2) = 0.023$  after scaling). An empirical TDS correction is applied and discussed.

Conventional least squares refinement was applied to the structure factors ( $R(L.O. \text{ data}) = 0.037$ ,  $R_w(L.O.) = 0.054$ ,  $G.O.F(L.O.) = 2.16$ ;  $R(H.O. \text{ data}) = 0.040$ ;  $R_w(H.O.) = 0.041$ ;  $G.O.F = 1.07$ ).

The iron-oxygen bond length contracts from 2.351 (3) Å at room temperature to 2.294 (2) Å at 120K corresponding to a higher binding of the axial THF ligands. Magnetic susceptibility measurements down to 10K show the absence of high spin-low spin transition.

The data sets are refined with the aspherical formalisms of Hansen and Coppens and of Hirshfeld and a comparison will be made.

The experimental d orbital occupancies calculated for iron from the deformation populations will be used to calculate the Mossbauer quadruple splitting.