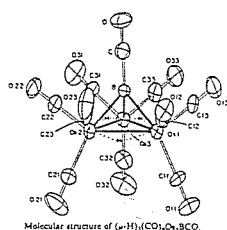


05.2-24 CRYSTAL AND ELECTRONIC STRUCTURE OF $(\mu\text{-H})_3(\text{CO})_9\text{Os}_3\text{BCO}$. By Leh-Yeh Hsu, Deng-Yang Jan and Sheldon G. Shore, Department of Chemistry, Ohio State University, Columbus, Ohio 43210, U.S.A.

The title compound (I) has been prepared and characterized by single-crystal X-ray diffraction as well as spectroscopic methods (^{13}C , ^{11}B , and ^1H NMR). The compound is a carbonyl borylidyne capped Os_3 triangle as shown in the figure.



The electronic structure of I has also been studied by using the Fenske-Hall quantum chemical approach with a fragment analysis in terms of the metal cluster $\text{H}_3(\text{CO})_9\text{Os}_3^+$ and capped ligand BCO. The calculation suggests that the apical boron is electron rich and the π system acts as an electron donor and electron acceptor. A localized MO description with a sp-hybridized boron forms a dative bond to the metal triangle and the remaining p orbitals form multi-centered π bonds to the Os_3 cluster.

The BCO unit in I has $\text{B-C}=1.469(15)\text{\AA}$ and $\text{C-O}=1.145(15)\text{\AA}$, while in H_3BCO (II) has $\text{B-C}=1.54\text{\AA}$ and $\text{C-O}=1.31\text{\AA}$. The CO stretching frequency is 2120 cm^{-1} in I and 2140 cm^{-1} in II. To explain this difference, nonparameterized Fenske-Hall molecular orbital calculations are carried out on both I and II with a fragment analysis in terms of $\text{H}_3(\text{CO})_9\text{Os}_3\text{B}$ and CO for the former, H_3B and CO for the latter. The calculation suggests that the back π bonding in I is more significant, due to the predominant movement of the electron density of the main Os_3B bonding orbitals to the CO π anti-bonding orbitals.

05.2-25 THE EFFECT OF CRYSTAL STRUCTURE AND PHASE STABILITY ON THE SUPERCONDUCTIVITY OF EQUIATOMIC TERNARY PNICTIDE COMPOUNDS* By G. P. Meisner, Los Alamos National Laboratory, MST-5, Los Alamos, NM 87545, USA.

The equiatomic ternary compounds $\text{MM}'\text{X}$ with $\text{M} = \text{Ti}$, Zr , or Hf , $\text{M}' = \text{Ru}$ or Os , and $\text{X} = \text{P}$ or As typically crystallize at high temperatures in the ZrRuSi -type hexagonal structure (P62m , M in 3(g), M' in 3(f), and X in 2(c) and 1(b)) and exhibit superconductivity at temperatures as high as 13.3 K for ZrRuP (Barz, Ku, Meisner, Fisk, and Matthias, Proc. Natl. Acad. Sci. USA (1980) 77, 3132; Meisner, Ku, and Barz, Mater. Res. Bull. (1983) 18, 983). These compounds are metastable and crystallize at low temperature in the TiNiSi -type or TiFeSi -type orthorhombic structures with $\text{X} = \text{P}$ or As , respectively. These three structures are all built from essentially the same crystal subunits. The TiNiSi -type structure (Shoemaker and Shoemaker, Acta Crystallogr. (1965) 18, 900) arises from a substantial re-arrangement of the subunits compared to the hexagonal structure yet superconductivity persists at the moderate temperature of 3.9 K for orthorhombic ZrRuP (Meisner and Ku, Appl. Phys. (1983) A31, 201). The TiFeSi -type structure is a superstructure of the hexagonal phase with very nearly the same arrangement of atoms (Jeitschko, Acta Crystallogr. (1970) B26, 815) but results in the disappearance of superconductivity in HfRuAs (Meisner, Phys. Lett. (1983) 96A, 483). The occurrence of the TiFeSi -type superstructure among the $\text{MM}'\text{X}$ ternary compounds with $\text{X} = \text{P}$, As , Si , or Ge correlates with Fe or Ru occupying the hexagonal 3(f) site and consequently the underlying distortion can be rationalized as a sharing of unpaired electrons between pairs of Fe or Ru atoms. The nature of the distortion suggests superconductivity originates with the $\text{M-M}'$ zig-zag chains which are present and undistorted in both superconducting modifications of ZrRuP but are distorted in the non-superconducting modification of HfRuAs .

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05.2-26 A COMPARISON OF THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE POLYMORPHS OF NEMATOGENIC 4,4'-BIS-(ETHOXY)AZOXYBENZENE. By C. E. Pfluger, Dept. of Chem., Syracuse University, Syracuse, N.Y., and R. D. Gilardi, and C. F. George, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C., USA.

The room temperature structures (22°C) of three crystal polymorphs of the compound 4,4'-bis(ethoxy)-azoxybenzene (also called p,p'-azoxydiphenetole), a compound exhibiting a nematic liquid crystalline phase from 137 to 168°C , as well as a low-temperature structure of the triclinic polymorph, have been determined. These structures represent the initial phase of a systematic variable temperature X-ray crystallographic study of several members of a homologous series (4,4'-bis(methoxy)-, 4,4'-bis(ethoxy)-, and 4,4'-bis(propoxy)-azoxybenzene) in an attempt to obtain information regarding the intra- and inter-molecular interactions which must account for the liquid crystalline behavior of this series of compounds. The isolation of three crystal polymorphs at room temperature presents an opportunity to compare the intra- and inter-molecular interactions for this nematogenic molecule in three different packing arrangements. A comparison of the low- and room-temperature structures has been useful in extracting atomic thermal motion information from the somewhat disordered crystal structure of the triclinic polymorph.

05.2-27

The study by electron microscopy of virgin crystals (Franco and Fernández-Ferrer, 1984) obtained by evaporation from a water solution, shows two kind of crystals, which we have identified by X-ray powder analysis; 46 relevant peaks of diagramme are indexed according to the cell parameters of structure of ferroelectric phase of TGS, and 41 with the cell parameters of switching fatigued structure.

The appearance of pyroelectric phase of TGS in the virgin crystals suggest the possibility to remove a crystal and refine, the previous crystal structure, because switching fatigued crystals show a lot of defects due to the aging process. The virgin pyroelectric phase has crystals with $a=9.190(6)$, $b=12.662(3)$, $c=5.751(7)$ $\beta=105.7(7)^\circ$ and refinement leads to $R=0.026$ ($R_w=0.033$).

In order to determine the different morphology of crystals, a study by Hartmann-Peardock theory has been carried out. A first result has been that the crystallization energy of ferroelectric phase is less than pyroelectric one. This suggest to use a method of crystallization in which the pyroelectric phase would not be obtained. Experimental results show that pyroelectric phase does not growth in low supersaturation, while it is obtained to higher values of supersaturation.