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Abstracts of Forthcoming Articles

Solid State Chemistry of Organic Polyvalent Iodine Compounds. V. The Crystal Structures of 3-oxo-3H-2, 1-benzoxiodol-1-yl o*-bromobenzoate (Two Polymorphs) and 3-oxo-3H-2, 1-benzoxiodol-1-yl* o*-chlorobenzoate.* J. Zanos Gougoutas and D. G. Naae. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Single crystal transformations of 2-iodo-2′-bromo-, and 2-iodo-2′-chlorodibenzoyl peroxides (*IIa* and *IIb*) yield topotactically aligned crystal structures of their respective isomers: 3-oxo-3H-2, 1-benzoxiodol-1-yl *o*-bromobenzoate (*Ia*) and its *o*-chlorobenzoate analog (*Ib*). Two of the polymorphic forms of *Ia* ($C_{14}H_8IBrO_4$) which are formed in crystalline *IIa* can also be obtained by crystallizing *Ia* from various solvents: (*Ia*–β), $a = 7.474$, $b = 13.994$, $c = 13.152$ Å, $\beta = 102.4°$, $Z = 4$, $P2_1/a$, and a disordered acicular form (*Ia*–α) which appears to be orthorhombic, $a = 3.99$, $b = 26.553$, $c = 26.008$, $Z = 8$ ($Pbc2_1$?). The only form of *Ib* ($C_{14}H_8IClO_4$) obtained by crystallizations from solvents is also formed in crystalline *Ib*. The crystal structures of the isostructural *Ia*–β and *Ib* have been determined but only the latter has been refined. ($R = 0.059$ for 2085 "observed" intensities.) The derivative crystal structure of *Ia*–α has been determined only in (100) projection ($R = 0.08$ for 156 observed intensities). The three structures contain similar chains of bimolecular units or "dimers." The "dimers" are analogous to those found in crystal structures of the benzoate, *m*-chlorobenzoate, *o*-iodobenzoate, and *o*-fluorobenzoate analogs of I. Novel polymorphs (X_a and X_b) of *Ia* and *Ib* are formed during the solid state peroxide isomerizations. The isostructural X_a and X_b consist of chains of "dimers" which are similar to those in *Ia* and *Ib*.

Solid State Chemistry of Organic Polyvalent Iodine Compounds. VI. The Crystal Structure and Topotactic Hydrolysis of 3-oxo-3H-2, 1-benzoxiodol-1-yl o*-fluorobenzoate.* J. Zanos Gougoutas, Kuo H. Chang, and M. C. Etter. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. The compound 3-oxo-3H-2, 1-benzoxiodol-1-yl *o*-fluorobenzoate (*IIIc*) is formed as a topotactically aligned crystal structure when single crystals of its dibenzoyl peroxide isomer thermally decompose at room temperature. Independently it has been found that single crystals of *IIIc* grown from solvents are hydrolyzed to *o*-iodosobenzoic acid, *II*, and *o*-fluorobenzoic acid after ~4 weeks in a moist atmosphere at ~45°C. *II* is formed topotactically in a conservatively twinned arrangement in which the (100) planes of the equally present twin members are parallel to (001) of *IIIc*. In addition, the 4 Å *b*-axes of the twin members align with the 4 Å *a*-axis of *IIIc*. Other examples of topotactic hydrolyses resulting in twinned arrangements of *II* are cited in reference to the novel possibility that the favored mode of alignment (the specific topotaxy between the reactant and *one* twin member) is one which, when augmented by conservative twinning, results in a favorable interphase between the conservatively twinned members. The transformation *IIIc* → *II* and more than 20 other corroborating examples of topotaxy in our studies lead us to expect the alignment of 4 Å axes whenever they are present in both the reactant and product of topotactic transformations involving comparable aromatic molecules. The crystal structure of *IIIc* ($C_{14}H_8IFO_4$), $a = 4.08$, $b = 12.00$, $c = 26.25$ Å, $\beta = 90.5°$, $Z = 4$, $P2_1/c$ (refined to $R = 0.10$ for 453 photographically recorded intensities) consists of chains of *transoid* "dimers" similar to those previously observed in structures of closely related derivatives.

$Ba_{15}Fe_7S_{25}$ and Ba_3FeS_5: Crystal Structures, Mössbauer, Magnetic and Electrical Behavior. J. T. Lemley, J. M. Jenks, J. T. Hoggins, Z. Eliezer, and H. Steinfink. Department of Chemical Engineering, The University of Texas, Austin, Texas 78712. $Ba_{15}Fe_7S_{25}$ is prepared by reacting stoichiometric amounts of BaS, Fe, and S in evacuated quartz ampoules while Ba_3FeS_5 is obtained in a tetrahedral press at 50 kbar and 1000°C. The crystal structure of $Ba_{15}Fe_7S_{25}$ has been determined using 4053 independent, nonzero X-ray reflections measured by a counter technique. The compound crystallizes in the orthorhombic system, $Pnma$, $a = 41.91(1)$ Å, $b = 9.572(3)$ Å, $c = 12.654(3)$ Å, $\rho_{calc} = 4.14$ g/cc, $z = 4$. In both compounds, Fe is tetrahedrally coordinated to S, and Ba is in either

9- or 8-fold coordination (trigonal prism with capped rectangular faces or cube). Ba–S distances are about 3.4 Å, Fe–S distances are 2.26 Å. In Ba_3FeS_5, single, isolated tetrahedra are present. In $Ba_{15}Fe_7S_{25}$ there are eight isolated trinuclear units, formed by a central tetrahedron sharing one edge and one corner, respectively, with two terminal tetrahedra, and four isolated single tetrahedra in the unit cell. The BaS_6 trigonal prisms form infinite columns by sharing the triangular faces. The columns share edges to form distorted hexagonal rings. Within the rings are additional S and Ba ions, and Fe in tetrahedral sites. The main difference between the two structures is the filling of the tetrahedral sites inside the hexagonal rings. The effective paramagnetic moment in $Ba_{15}Fe_7S_{25}$ is 5.5 μ_B in good agreement with a value expected from 6 Fe^{3+} and Fe^{2+} from the stoichiometry. The room temperature Mössbauer spectrum shows isomer shifts of 0.2 mm/sec. The data indicate that electron delocalization occurs across the edge-shared tetrahedra so that an effective charge distribution $5Fe^{3+}$ and $2Fe^{+2.5}$ is present. The material has a room temperature electrical resistivity of 10^5 ohm/cm. The effective magnetic moment for Ba_3FeS_5 is 5.1 μ_B as might be expected for Fe^{2+} or Fe^{4+}. One quadrupole-split Mössbauer spectrum is observed with an isomer shift of 0.2 mm/sec, a value usually observed for Fe^{3+}. The observations are reconciled by postulating the delocalization of an electron within the tetrahedral configuration. The room temperature electrical resistivity is 10^5 ohm/cm.

Observation Directe par Microscopie Electronique a Haute Resolution de la Transformation des Hydroxycarbonates de Terres Rares (Type B) en Oxycarbonates (Type II). H. Dexpert, G. Schiffmacher, and P. Caro. Laboratoire des Terres Rares, 1, Place Aristide Briand, 92190 Meudon-Bellevue, France. Type *B* rare earth hydroxycarbonate $(LnOH)CO_3$ is a lamellar hexagonal structure isomorphous to bastnaesite $(LnFCO_3)$. Type II oxycarbonate $(LnO)_2CO_3$ is another hexagonal lamellar structure built on an $(LnO)_n^{n+}$ complex cation of ternary symmetry. Lattice images were obtained for both compounds directly exhibiting the lamellar character. The thermal decomposition of the hydroxycarbonate into the oxycarbonate was followed in the electron microscope. The transition is topotactic and the crystallographic orientations were determined. The two compounds may have their triad axes and the $[1\bar{1}0]$ (hydroxycarbonate) and [010] (oxycarbonate) axes in common, or the two triad axes may be parallel and the lamellar structures merge together. The oxycarbonate appears then in the form of bubbles in the hydroxycarbonate matrix, because of a slight deficiency (12 to 14) in the number of rare earth atom planes for the same distance along the triad axes for the oxycarbonate versus the hydroxycarbonate.

Identification of Binary Compounds in the System Ce_2O_3–WO_3. M. Yoshimura, F. Sibieude, A. Rouanet, and M. Foex. Laboratoire des Ultra-Refractaires, Odeillo, 66120 Font-Romeu, France. The system CeO_2–Ce_2O_3–WO_3 and Ce_2O_3–WO_3–W are studied at high temperature. Six compounds were found as stable phases in the system Ce_2O_3–WO_3. The compound $3Ce_2O_3 \cdot WO_3$ has a fluorite-like cubic structure of $a_o = 11.040$ Å and forms solid solutions with constituent oxides or CeO_2. The compound $3Ce_2O_3 \cdot 2WO_3$, which seems to be isostructural with $3La_2O_3 \cdot 2WO_3$, is stable only in the temperature range of 1545 ~ 1730°C. The compound $Ce_2O_3 \cdot WO_3$, which has a monoclinic structure, transforms reversibly at 1360°C to a tetragonal structure with the cell parameters $a_o = 5.469$ Å, $c_o = 8.790$ Å. The compound $Ce_2O_3 \cdot 2WO_3$, identified as monoclinic, also has a reversible transformation at 1105°C. It high-temperature phase has a cubic cell with the cell parameter $a = 7.046$ Å. As is well known, $Ce_2O_3 \cdot 3WO_3$ appeared to have a high-temperature behavior similar to that of $La_2O_3 \cdot 3WO_3$. The compound $2Ce_2O_3 \cdot 9WO_3$, whose structure could not be analyzed, melts congruently at 1026°C.

On the Formation of $FeSe_2$ Single Crystals by Chemical Transport Reactions. J. Pickardt, B. Reuter, E. Riedel, and J. Söchtig. Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, 1 Berlin 12, Germany. The formation of synthetic ferroselite single crystals, $FeSe_2$, during chemical transport experiments in the system Fe–Cr–Se was observed. The crystals are orthorhombic, $a = 4.804(2)$, $b = 5.784(3)$, and $c = 3.586(2)$ Å. They were characterized by X-ray structure analysis and refined atom parameters are reported.

Evidence for the Existence of Iron Tungsten Bronzes. I. J. McColm and R. J. D. Tilley. School of Materials Science, University of Bradford, Bradford BD7 1DP, Yorkshire, England. C. P. M. Barton and N. N. Greenwood. Department of Inorganic and Structural Chemistry, University of Leeds,