

NEW INTERCALATION COMPOUNDS OF C₆₀ WITH ETHENE AND ETHANEC. Wilson¹ A.S. O'Neil¹ A.J. Blake¹ M. Poliakoff¹ A.E. Goeta² J.A.K. Howard²¹University of Nottingham School of Chemistry University Park NOTTINGHAM NG7 2RD UK²Dept. of Chemistry, University of Durham, Durham, DH1 3LE, UK

Previously unseen intercalation compounds of C₆₀ with small hydrocarbons have been prepared using supercritical anti-solvent techniques. These compounds are of interest as potential gas storage media [Gadd et al, Fullerene Sci Technol., 7, 1043 (1999); Science, 2777, 9333, (1997)].

C₆₀ intercalates of small gas molecules have been generated through hot isostatic pressing typically involving pressures in excess of 1.5 GPa and temperatures > 500°C. Single crystal data for these intercalates has been virtually impossible to obtain previously. Solvent containing fullerene compounds of a wide range of systems are known, usually with several molecules of solvent per C₆₀ and a major rearrangement of the crystal lattice [Dyachenko and Graja, Fullerene Sci. Technol., 7, 317, (1999)].

The use of supercritical anti-solvents for precipitation of C₆₀ intercalation compounds fills a gap between these small gas and large solvent molecule intercalates for materials too large and thermally unstable to be intercalated as a gas but with too low a boiling point and solubility for C₆₀ to be intercalated as a solvent intercalate [C.N. Field et al, J. Am. Chem. Soc., 122, 2480 (2000)]. New ethene (C₂H₄) and ethane (C₂H₆) intercalates have been generated using this technique. X-ray crystallographic data collected at 150 and 35 K show the ethene intercalate is in space group *Pa*-3, *a* = 14.155(3) Å at 150K. The ethane intercalate crystallizes in a primitive tetragonal space group with *a* = 9.8420(11) Å, *c* = 14.796(2) Å at 150 K.

Keywords: FULLERENE INTERCALATES SUPERCRITICAL FLUIDS

ABIOTIC STRUCTURES OF SOLID BITUMEN AS BIOLOGICAL SYSTEMS PREDECESSORS AND HYDROCARBON CRYSTALLIZATION OF LIFE

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The mineral world coexists in nature with the world of ordered hydrocarbons. In spite of the fact, that study of supermolecular ordering in solid hydrocarbons is at its dawn, non-biogenic hydrocarbon organism-like forms have been found in many earthly and space objects. One prominent example is fibrous kerite crystals from crystallization voids in pegmatites. Kerite crystals show fibrous and cylindrical habits, frequently with spheres at the ends and an internal axial channel. Spiral-like individuals twisted in one direction (left or right; chiral selection is carried out according to the epitaxial mechanism). Fibrous kerite crystals have elemental composition nearly identical to that of protein. They contain all chemical elements typical of the living matter and all elements-catalysts. Heating the crystals in the range from twenty to six hundred Celsius resulted in release of a variety of hydrocarbon gases to the inner channels and environment. The crystals are distinguished by anomalously high contents of all protein amino acids, which are synthesized, from abiogenic components during crystallization. Protein self-assembly and evolution of some organismic functions described as biological ones are possible. We relied on fibrous kerite crystals to develop a model of a probiological organism, genetic predecessor of biological life forms and to propose a concept of hydrocarbon crystallization of life. Life originated and evolved as a single whole, an integral sequence of crystallization processes occurring in complex hydrocarbon systems, not as a result of random events and combination of genetically different components. Both minerals and organisms evolve governed by common ontogenetic laws.

Keywords: HYDROCARBON CRYSTALS, PROTOBIOLOGICAL ORGANISMS, CRYSTALLIZATION OF LIFE

AN IRON(II) SPIN-CROSSOVER COMPLEX: A VARIABLE TEMPERATURE CRYSTALLOGRAPHIC STUDY

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Iron(II) complexes undergoing spin-crossover transitions are of interest due to applications as molecular switches or materials for information storage. As the low spin state is often stable only at very low temperatures much research has focused on finding materials in which the transition occurs near enough to ambient temperature to be practically useful. Spin-crossover transitions can be caused by light, temperature and pressure and the existence of long and short range interactions can lead to cooperative spin transitions, as seen in [CuL₂][BF₄]₂ (I) (L = 2,6-di(pyrazol-1-yl)pyridine). [FeL₂][BF₄]₂ (II) has been shown to undergo a thermal spin crossover transition with a width of 3K centered at 259K which may be mediated by an order-disorder transition of the BF₄⁻ anions. This relatively high transition temperature coupled with the narrow transition width renders (II) particularly well suited for the applications mentioned above.

A variable temperature crystallographic study of the structure of compound (II) was carried out over a range of temperatures from 290 to 30K. The results illustrate the structure of the compound before and after the spin-crossover transition, showing a large decrease of 3.7% in the cell parameter in the crystallographic *c*-direction and the ordering on cooling of the BF₄⁻ anions.

References

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STUDY OF NEW COMPLEXES OF LANTHANIDE NITRATES WITH HEXAMETHYLENETETRAMINE

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We have investigated complex salts of lanthanides with Cl⁻, Br⁻, NCS⁻ and hexamethylenetetramine, (CH₂)₆n₄ (hmta, urotropin) with various degrees of hydration. The thermal decomposition of these compounds have been investigated and mechanism of the thermal dehydration reactions established¹. The IR and Raman spectra of the salts with various degree of hydration have been analyzed². The crystal structure of [Nd(NO₃)₂ · (H₂O)₆]²⁺ · (NO₃)₃ · 2(CH₂)₆n₄ · 3H₂O (i) has been solved previously³. Here, we report the crystal and molecular structures of five new complexes of lanthanide nitrates with hmta of two general formulae: [Ln(NO₃)(H₂O)₇]²⁺ · 2(NO₃)₃ · 2hmta · 3H₂O [where Ln = Eu or Gd, (ii) & (iii) resp.], and [Ln(H₂O)₈]³⁺ · 3(NO₃)₃ · 2hmta · 3H₂O [where Ln = Dy, Ho or Er, (iv), (v) & (vi) resp.]. The complexes (ii) & (iii) are monoclinic, crystallize in space group *P*₂₁/*c* and are isostructural. The complexes (iv), (v) & (vi) are triclinic, space groups *P*-1 and are isostructural too. The volumes of the unit cells decrease for the compounds (iv), (v), and (vi) (*v* = 1530.19, 1525.09, and 1516.59 Å³ resp). This work was financed by the State Committee of Scientific Research, Warsaw, Poland, contract no. 1512/09/2001/21.

References

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