

- Part I. Clathrasil Chemistry: Synthesis and Characterization of Dodecasil-3C and Dodecasil-1H Clathrasils
- Part II. Synthesis and Structure of Pentamethylcyclopentadienylrhodium Vanadium and Molybdenum Oxides

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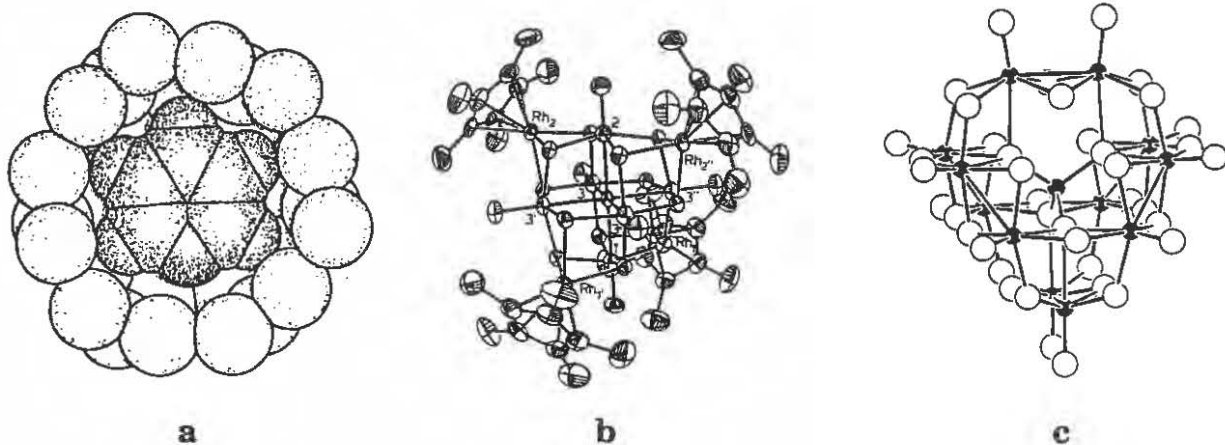
Part I

Quartz, the crystalline SiO_2 polymorph stable at ambient temperature, is a useful piezoelectric material grown in large single crystals by hydrothermal methods [1]. Clathrasils are crystalline silica inclusion compounds $n \text{SiO}_2 \cdot \text{M}$, comprised of a three-dimensional silica host framework containing cages that encapsulate organic molecules, M [2]. Clathrasils can be regarded as derivatives of quartz. Since a variety of host frameworks and guest molecules can be manipulated to form clathrasils, there exists an enormous potential for use of clathrasil crystals in optical and electronic applications.

Although various phases of clathrasils have been synthesized hydrothermally, they are known only as small, inhomogeneous, single crystals [3]. The effect of various guest molecules and impurities on the physical properties of clathrasils has been relatively unexplored. The goal of this work has primarily been to develop a protocol for the synthesis and characterization of large, chemically pure single crystals of clathrasils. The incorporation of a series of guest molecules into a given silica host framework was attempted in order to investigate the influence of the organic guest molecule on the phase transition behavior of the clathrasil.

Hydrothermal methods were developed for the growth of mm-sized crystals of dodecasil-3C clathrasils, $17 \text{SiO}_2 \cdot \text{M}$ (M=pyridine, cyclopentane, cyclohexane, piperidine, pyrrolidine, cyclopentylamine and cyclobutylamine) [4]. By systematically varying the silica source, guest molecule and/or catalyst concentrations, reaction conditions were optimized for large, chemically pure dodecasil-3C (D3C) crystals. Fumed silica served as a good silica source, yielding crystals which were shown by solid state ^{29}Si and ^{13}C CPMAS NMR spectroscopy to be of high purity. For the synthesis of pyridine, cyclopentane and cyclohexane D3C crystals, an aqueous pyridinium bifluoride solution was used as a catalyst [5]. Phase transformations of pyridine D3C crystals were determined by differential scanning calorimetry commencing at 161 °C and -46 °C on cooling. The domain configurations during the phase transitions of Py-D3C were observed by variable-temperature optical microscopy. The phase transformations of Py-D3C corresponded with a change of variable-temperature X-ray powder patterns, ^{29}Si and ^2H NMR spectra. The crystal structure of the ambient temperature tetragonal $17 \text{SiO}_2 \cdot \text{C}_5\text{H}_5\text{N}$ phase, shown in a space-filling model **a**, revealed that the Py-D3C crystals were acentric at ambient temperature and thus second harmonic generators. All other clathrasils synthesized were also tetragonal at ambient temperature, and underwent a transformation to a cubic phase at elevated temperatures, as well as a transformation to a lower symmetry phase at lower temperatures. The size of the guest molecule had a large influence on the phase transition temperatures, with larger guest molecules raising the temperature of the high temperature transition and lowering the temperature for the lower temperature transition.

The synthesis of dodecasil-1H (D1H) has been relatively unexplored compared with that of D3C [6]. The methodology for synthesizing large D3C crystals was applied to form the dodecasil-1H phase with adamantane. Adamantane D1H crystals were founded by X-ray diffractometry, solid state ^{13}C and ^{29}Si NMR spectroscopy to be of high purity.



Part II

A number of organometal oxo compounds have been obtained from known organometallic complexes and existing or preformed polyoxoanion salts by simple metathesis reactions [7]. Since the types of compounds prepared reflect the synthetic approach employed, alternative routes could be considered. This research was initiated by reacting a known organometal hydroxide with a simple metal oxide in water. The reaction of $[(C_5Me_5)Rh(OH)_2]_2$ with V_2O_5 in water has yielded $[(C_5Me_5)Rh]_4(V_6O_{19})$ (**b**) [8]. The crystal structure of **b**, revealed the presence of a neutral complex in which four Cp^*Rh^{2+} cations are bound to a single $V_6O_{19}^{8-}$ anion. The 1H and ^{13}C NMR spectroscopy of **b** indicated that all four Cp^* rings in the cluster are magnetically equivalent. The ^{51}V NMR spectrum is consistent with the structure for **b**. This approach can be extended to the synthesis of $\{[(C_5Me_5)Rh]_8-Mo_{13}O_{40}\}Cl_2$ by the hydrothermal reaction of $[(Cp^*Rh)_2(OH)_3]Cl$ with $MoO_3 \cdot 2H_2O$ [9]. In this crystal structure, each of the eight Cp^*Rh^{2+} cations is bound to three of the twenty-four doubly bridging oxygens of a $Mo_{13}O_{40}^{14-}$ anion. The $Mo_{13}O_{40}^{14-}$ core (**c**) has the same structure as the isopolyoxocation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ which was known as an ϵ -Keggin isomer [10]. The structure of **c** was confirmed by 1H and ^{13}C NMR spectroscopy.

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