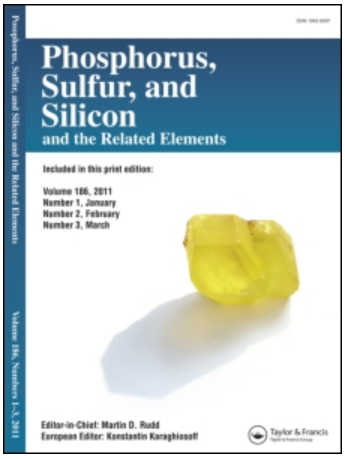

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Cyclic Aluminophosphinate: Molecular Structure, and Solid-State Multinuclear NMR Study

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We present a new Al-O-P cyclic aluminophosphinate characterized by single X-ray diffraction (XRD) and multinuclear solid state NMR.

Keywords: Inorganic ring; SBU; Solid-state NMR; Cross Polarisation; ^{27}Al

INTRODUCTION

Synthesis of clusters which are secondary bulding units (SBU) of microporous materials is now fully developed [1]. They could be used in an alternative way to synthesize microporous materials. These materials, which are intensively studied, due to their catalyst properties,

are synthesized generally by a thermal or solvothermal pathway, using organic molecules as structure directing agent. These syntheses methods do not allow to predic the structure of the final material. This drawback could be advantageously circumvented by using clusters, with cores mimicking SBU's of microprous materials. The porosity of the desired material would be determined by the shape of the starting clusters.

Whereas aluminophosphate microporous materials were intensively studied by multinuclear solid-state NMR, clusters SBU analogues were , surprisingly, never investigated by these techniques. Studying such kind of clusters by solid-state NMR is very promising because of the relationship between the NMR results and the local structure around the studied nucleus [2]. These results are a perfect starting point to the study of syntheses using the building block strategy.

STRUCTURE

We present the compound $[Al_2(C_6H_5HPO_2)_2(C_4H_9OH)_8]Cl_4$ characterized by single-cristal XRD (Figure 1). The core of the cluster is a cyclic $[Al_2P_2O_4]$ unit, mimicking a S4R (Single Four Ring) unit of microporous materials. Aluminum atoms are octahedrally coordinated to six oxygen atoms. Two Al-O-P bounds and four butanol molecules are involved. Phosphorus atoms are surrounded by two oxygens atoms, a phenyl group and an hydrogen atom. Exact location of protons could

not be determined by XRD. Furthermore, four chlorine atoms are located between the rings.

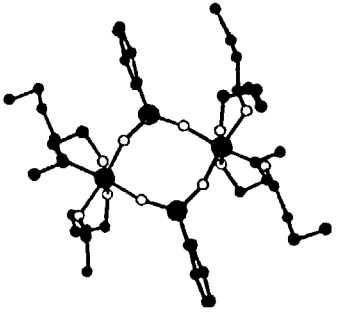

FIGURE 1 : $[Al_2(C_6H_5HPO_2)_2(C_4H_9OH)_8]Cl_4$.
Red : P ; blue : Al ; green : O ; black : C. Cl atoms are omitted.
See Color Plate IV at the back of this issue.

SOLID-STATE NMR

^{27}Al is a quadrupolar nucleus (I=5/2) subjected to a second order quadrupolar effect [3]. This effect, which is not completely averaged by MAS, implies complex, broad but charasteristic lineshapes. The simulation of the central transition of the ^{27}Al MAS spectrum of the cyclic cluster (Figure 2) allows the determination of the isotropic chemical shift (δ_{ISO}=-2,51 ppm) in agreement with the octahedric symmetry of the aluminum atom, and the quadrupolar parametrers (quadrupolar constant C_Q=3 MHz, asymmetry parameter η_Q=0.25). It is worth noting that the center of gravity of the <±1/2;±3/2> transitions, can be observed (* in Figure 2) : this observation is quite unique.

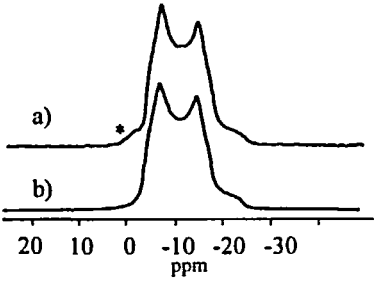

FIGURE 2: a) Central transition of the cyclic cluster (^{27}Al MAS spectrum). * : <±1/2;±3/2> transitions center of gravity.
b) Simulation using C_Q=3 MHz and η_Q=0.25.

The cluster was also studied by ^{31}P Cross Polarisation NMR. The carefull observation of the dynamic polarisation transfer from ^{1}H to ^{31}P at a spinning rate of 5 kHz reveals oscillations, which are characteristic for the existence of the spin pair ^{1}H-^{31}P [4]. The same experiment done at 14 kHz on the phosphorus precursor of the cyclic cluster (phenyl phosphinic acid) allows us to estimate the ^{1}H-^{31}H distance (1,53 Å). The same experiment will be done on the cluster, and such a distance is expected.

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