Low-temperature Syntheses of a 1,4-Diazabicyclo[2.2.2]-octane-intercalated Phosphatoantimonic Acid

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Hydrothermal syntheses in the presence of 1,4-diazabicyclo[2.2.2]octane (dabco) have been undertaken in the antimony phosphate system, giving dabco-intercalated phosphatoantimonic acid with $[\{Sb_3O_6(PO_4)_2\}_n]^{3n-}$ layers similar to those in $K_3[Sb_3O_6(PO_4)_2]\cdot 5H_2O$. The same material can be prepared by titration of the layered phosphatoantimonic acid $H_3Sb_3O_6(PO_4)_2\cdot xH_2O$ **1** with a dabco solution. It corresponds to the intercalation of 1 mol of dabco per mol of **1**, *i.e.* a neutralization of 2/3 of the acidity. The compound $H_3Sb_3O_6(PO_4)_2(dabco)\cdot 4H_2O$ has been analysed and characterized by thermal analysis, X-ray diffraction, IR and MAS NMR spectroscopies (^1H, ^{31}P). A structural model is proposed.

Zeolites, as well as other microporous solids such as aluminophosphates, find use in such diverse processes as separations, ion exchange and catalysis.[1-3] These materials, containing anionic frameworks made from p-block elements with mainly tetrahedral co-ordination, are synthesized hydrothermally in the presence of templating cations or molecular species. Similar solids with mixed octahedral–tetrahedral frameworks and large organic cation-filled cavities have recently been prepared, under hydrothermal conditions, in the molybdenum phosphate system[4] and 'such compounds represent the beginning steps toward materials that could combine the exquisite shape-selective absorptivities of the zeolites with the reactivity of d-block elements'. More generally, their preparation opens the way to a new class of synthetic microporous octahedral–tetrahedral framework solids. As part of a search for similar solids, investigations under hydrothermal conditions have been undertaken in the antimony phosphate system. The first compound which has been identified has a layered structure with $[\{Sb_3O_6(PO_4)_2\}_n]^{3n-}$ layers and a protonated form of 1,4-diazabicyclo[2.2.2]octane (dabco) in the interlayer space. Such anionic layers have already been observed in $K_3[Sb_3O_6(PO_4)_2]\cdot 5H_2O$,[5,6] a material prepared by solid-state reaction at about 1000 °C, and which can be ion-exchanged in acidic media, near room temperature, thus leading to the layered phosphatoantimonic acid $H_3Sb_3O_6(PO_4)_2\cdot xH_2O$.[7-9] This new inorganic acid behaves as a good ion exchanger[7] and as a host for intercalated amines, like dabco, within the interlayer space. A dabco-intercalated phosphatoantimonic acid with $[\{Sb_3O_6(PO_4)_2\}_n]^{3n-}$ layers can then be prepared *via* two very different routes which will be described here. This paper also reports characterization studies of this compound including thermal analysis, X-ray diffraction, IR and magic angle spinning (MAS) NMR spectroscopies (^1H, ^{31}P).

Experimental

Hydrothermal Synthesis.—The starting materials were H_3PO_4 (p.a. Prolabo), dabco (Aldrich, 98% purity) and a freshly prepared solution of antimonic acid, usually denoted $(HSbO_3)\alpha$.[10] The latter was obtained by passing an aqueous $K[Sb(OH)_6]$ solution (38 mmol dm^{-3}) over a strong cation-exchange resin in the H^+ form (Dowex 50W-X2). A mixture of the reactants antimonic acid : H_3PO_4 : dabco in the ratio 1 : 1 : 0.5 and a large excess of water (molar ratio water : dabco *ca.* 10^4 : 1) was placed in a stainless-steel autoclave lined with Teflon and heated at 180 °C for 6 d. The resulting product was filtered off, washed with distilled water and acetone, and dried at room temperature under vacuum.

Titration of $H_3Sb_3O_6(PO_4)_2\cdot xH_2O$ **1** *with dabco.*—The layered phosphatoantimonic acid **1** was prepared as previously described.[6] The x value of this material, kept in an atmosphere with a controlled relative humidity of 35%, was 6 which corresponds to a theoretical exchange capacity of 3.94 mequivalents g^{-1}.[8] Titrations were performed using a microprocessor-based autotitrator (Metrohm-titrino SM 702) which allows many possibilities of dosing modes with fixed or variable titration rates. In the experiments distilled water (20 cm^3) was added to the layered acid (100 mg) and a 0.1 mol dm^{-3} dabco solution was added at a rate which does not influence the shape of the titration curve.

Thermal and X-Ray Analyses.—Thermal analyses were performed on a Perkin-Elmer model TGS-2 thermal gravimetric analysis (TGA) system at a heating rate of 60 K h^{-1} in air. The dehydration process, as well as the loss (or decomposition) of dabco, was also followed by X-ray experiments at fixed temperatures with use of a D5000 Siemens powder diffractometer. In order to analyse the species lost by the sample during the thermal treatment, a 5989A Hewlett-Packard mass spectrometer was used up to 300 °C (limit of the equipment). Such experiments were performed under vacuum, which shifts thermal phenomena to lower temperatures. A TGA experiment was performed under similar conditions.

Infrared and MAS NMR Measurements.—The infrared absorption spectra (4000–400 cm^{-1}) were obtained with a Nicolet 20 SX FTIR spectrometer and KBr pellets. The ^{31}P and ^1H NMR spectra were acquired under conditions of single irradiation under magic angle spinning, using a Bruker MSL 300 spectrometer.

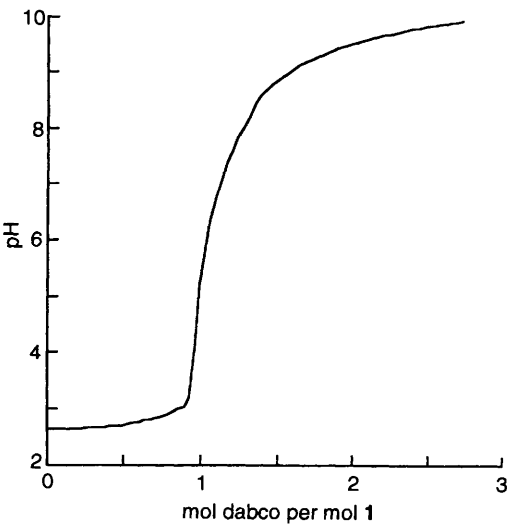

Fig. 1 Titration curve of compound **1** with a dabco solution

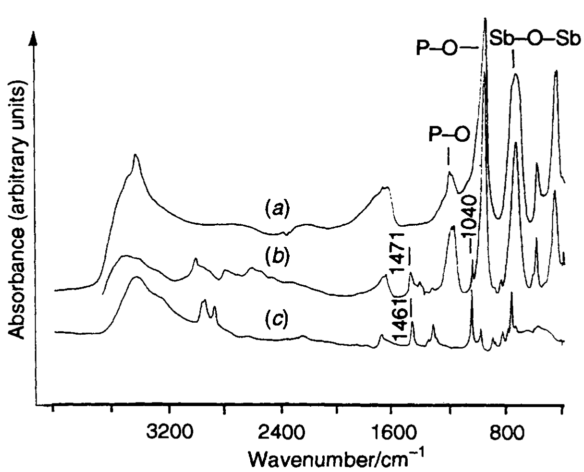

Fig. 2 Infrared absorption spectra of the compounds **1** (*a*), **1**•dabco (*b*) and dabco (*c*)

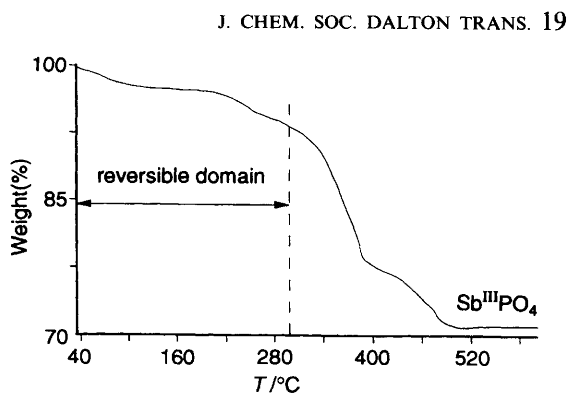

Fig. 3 The TGA curve for **1**•dabco

Table 1 Proton chemical shifts and relative intensities of the resonance lines [300.13 MHz, MAS spinning speed 15 kHz, reference $SiMe_4$ (δ 0)]

Compound	$\delta(^1H)$	Relative intensity (%)
1	9.25	
dabco	2.64	
1•dabco	8.30	8
	7.47	40
	3.67	52

Results and Discussion

Chemical Composition.—Fig. 1 shows the titration curve of compound **1** with dabco. One end-point is observed corresponding to the intercalation of 1 mol of dabco per mol of **1**, *i.e.* a neutralization of 2/3 of the acidity.

Materials prepared by the two methods, hydrothermal synthesis and titration, were analysed for their antimony, phosphorus, hydrogen, carbon and nitrogen contents by the CNRS Analysis Laboratory at Vernaison. Both compounds exhibit the same chemical composition: $C_6H_{23}N_2O_{18}P_2Sb_3$ (Found: C, 8.50; H, 2.75; N, 3.30; P, 7.25. Calc.: C, 8.60; H, 2.75; N, 3.35; P, 7.40%). Referring to Fig. 1, this corresponds to the end-point in the titration curve, *i.e.* 1 mol dabco per mol of **1**.

Infrared and X-Ray Diffraction Studies.—Both materials exhibit the same X-ray powder diffraction (XRD) pattern and the same IR spectrum. The XRD pattern is closely related to that of compound **1** thus indicating that the $[\{Sb_3O_6(PO_4)_2\}_n]^{3n-}$ covalent layers in **1** are present in both materials. However, as in the case of **1**,[7] the diffraction peaks are rather broad and their number is too small for any determination of the structure. The first reflection is rather intense; it represents an interlayer spacing (10.4 Å) almost identical to that observed in the potassium phase $K_3[Sb_3O_6(PO_4)_2]{\cdot}5H_2O$.

A vibrational study of compound **1** was done[9] at 20 °C in comparison with the parent potassium salt for which the observed frequencies have been assigned,[11] particularly for the P–O and Sb–O bond stretches. In the case of $K_3[Sb_3O_6(PO_4)_2]{\cdot}5H_2O$ this assignment is supported by a normal coordinate analysis.[12] The IR spectrum (Fig. 2) of the present materials with dabco clearly shows all the vibrations characteristic of the $[\{Sb_3O_6(PO_4)_2\}_n]^{3n-}$ layers in **1** superimposed on those of dabco. Furthermore, the $\delta(CH_2)$ band observed at 1461 cm⁻¹ for dabco is shifted to 1471 cm⁻¹ for **1**•dabco thus indicating that the amine is in a protonated form.[13]

Thermal Behaviour.—Fig. 3 shows the TGA curve. The weight loss, which occurs in two steps between 30 and 290 °C, corresponds to the dehydration process as revealed by mass spectrometry. However, the end of this process is not characterized by a clearly defined plateau. The water loss is reversible; it corresponds to four molecules per formula unit defined as $H_3Sb_3O_6(PO_4)_2(dabco){\cdot}4H_2O$ and is in good agreement with that inferred from the chemical analysis. When the temperature is increased above 290 °C dabco is gradually evolved from the material which becomes amorphous. Furthermore a complex 'redox' process occurs between nitrogen (from dabco) and antimony; the covalent layers are destroyed and at 500 °C the XRD pattern of $Sb^{III}PO_4$ is observed.

MAS NMR Studies.—The **1**•dabco compounds prepared using both synthetic methods present the same ^1H and ^{31}P NMR spectra. Results from ^1H MAS NMR investigations on **1**, dabco and **1**•dabco are presented in Table 1. In agreement with the chemical formula, **1**•dabco exhibits three distinct ^1H resonances, distinguishable by their relative intensities and chemical shifts. The chemical shift from the CH_2 groups in **1**•dabco is δ 3.67 whereas it is only δ 2.64 for free dabco. This result clearly indicates that the amine is protonated in **1**•dabco; correspondingly the chemical shift of two out of three acidic protons is lowered from δ 9.25 for **1** to δ 8.30 for **1**•dabco. The last (not titrated) proton is less acidic and cannot be distinguished from protons of the four water molecules.

Table 2 presents the ^{31}P MAS NMR spectral data for compounds **1** and **1**•dabco. The former possesses two distinct ^{31}P resonances in its spectrum, separated by 2.8 ppm. The same situation occurs for $K_3[Sb_3O_6(PO_4)_2]{\cdot}5H_2O$ although there is a unique crystallographic phosphorus site in its structure. This is due to the fact that neighbouring K^+ sites in the interlayer space are not fully occupied, which induces some local differentiation of phosphorus sites. It is very likely that H^+-

Table 2 Phosphorus-31 chemical shifts and relative intensities of the resonance lines [121.5 MHz, MAS spinning speed 10 kHz, reference 85% H_3PO_4 (δ 0)]

Compound	δ(^{31}P)	Relative intensity (%)
1	(a) −10.6	69
	(b) −13.4	30
1·dabco	(a) −16.8	5
	(b) −14.5	18
	(c) −13.0	22
	(d) −11.7	26
	(e) −10.2	29

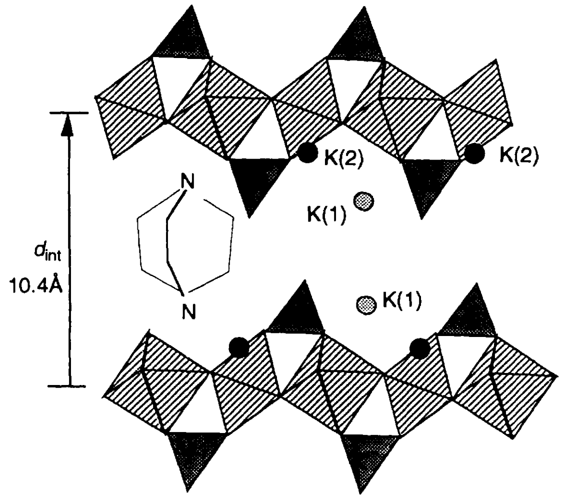

Fig. 4 Projection on (110) of two $[\{Sb_3O_6(PO_4)_2\}_n]^{3n-}$ covalent layers showing potassium sites in the parent phase and the postulated position for dabco in **1**·dabco

$(H_2O)_x$ species in **1** are responsible for a similar differentiation. For **1**·dabco there are five lines (labelled a–e in Table 2). Line a with a chemical shift of δ −16.8 could be attributed to P atoms at the surface of the sample. Indeed, the intercalation of dabco in **1** induces a large increase in the surface area, from ≈2 m^2 g^{-1} in **1** to ≈60 m^2 g^{-1} in **1**·dabco. Consequently the proportion of PO_4 groups at the surface of the material is no longer negligible (≈9%) and gives rise to a distinct line. Lines b and d on the one hand and c and e on the other are separated by 2.8 ppm, which is identical to the separation between the ^{31}P lines of **1**. That there are four lines for **1**·dabco instead of two for **1** and $K_3[Sb_3O_6(PO_4)_2]\cdot 5H_2O$ is probably related to the fact that there are two types of cations in the interlayer space of **1**·dabco: protonated dabco and $H^+(H_2O)_x$. This induces a further doubling of the differentiation observed in **1**.

Structural Model for **1**·dabco.—As already mentioned, the interlayer distance in **1**·dabco is very close to that of $K_3[Sb_3O_6(PO_4)_2]\cdot 5H_2O$.[5,6] The structure of the latter compound contains two potassium sites, K(1) and K(2) (Fig. 4), with the same multiplicity and statistically occupied at an average of 75%. Within the interlayer space, owing to the presence of water molecules (not shown in Fig. 4), two adjacent K(1) sites are separated by a distance which is close to the N···N distance in dabco. In **1**·dabco the dabco molecule could be perpendicular to the layers, as indicated in Fig. 4, with N atoms close to the K(1) sites. At this point it is important to consider why it is not possible to titrate the remaining $H^+(H_2O)_x$ with dabco. Indeed, if (for purposes of simplification) one defines the anionic layer to be delimited by two parallel planes, the surface per negative charge is 30 Å^2 in **1**; since the cross-section of dabco (perpendicular to the N···N axis) is ≈28 Å^2 it should be possible to titrate all the acidity. However, if the position suggested above for dabco in **1**·dabco is taken into account, the remaining $H^+(H_2O)_x$ would 50% occupy a position close to K(2). These acidic sites are then too far from each other to enable symmetrical protonation of additional dabco; nevertheless, they are still acidic as indicated by the chemical shift (δ 7.47) and by the fact that this remaining acidity can be titrated by a KOH solution leading to $K(H_2dabco)Sb_3O_6(PO_4)_2\cdot xH_2O$.

According to our structural model, in which protonated dabco occupies all pairs of adjacent K(1) sites, all the PO_4 groups are surrounded in the same way by dabco. However, with respect to the remaining $H^+(H_2O)_x$ 50% occupying a position close to the K(2) sites, there are two distinguishable PO_4 groups in equal proportions, which induces a splitting of the resonance lines observed in the ^{31}P NMR spectrum of compound **1**.

Conclusion

A dabco-intercalated phosphatoantimonic acid with $[\{Sb_3O_6(PO_4)_2\}_n]^{3n-}$ covalent layers has been prepared *via* two different routes: hydrothermal synthesis in the presence of templating cations and titration of compound **1** with a dabco solution. It has been analysed and characterized with the use of various techniques. X-Ray and MAS NMR investigations allow a structural model to be proposed.

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