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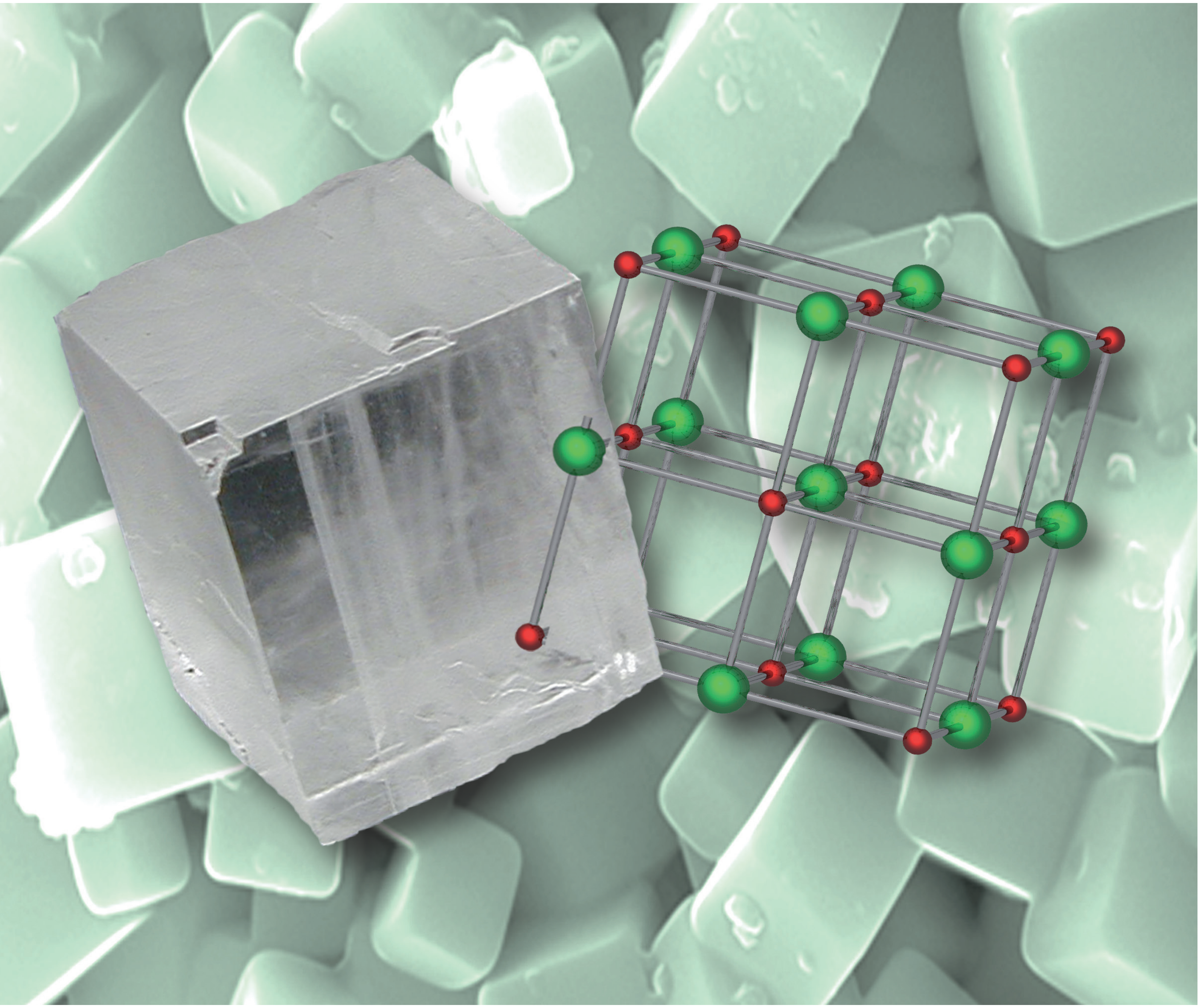

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A facile synthesis of dispersable NaCl nanocrystals

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During the classical malonic ester synthesis, sodium chloride is eliminated. Sodium diethyl malonate was reacted either with phenacyl chloride or acetyl chloride, both in toluene solution and without solvent. NaCl nanocrystals with a size of 100–300 nm were obtained that could be easily redispersed in organic solvents if phenacyl chloride was used as reagent. The dispersion in dichloromethane was stable for at least two weeks without sedimentation or agglomeration.

Introduction

The preparation of nanoparticles can be accomplished by "top-down" (physical) and by "bottom-up" (chemical) syntheses.[1,2] In chemical syntheses, a typical approach is the formation of water-insoluble compounds like metals (*e.g.* Au, Ag) or semiconductors (*e.g.* ZnS, CdS) by a suitable chemical reaction. However, this is difficult for easily water-soluble compounds like NaCl due to their high solubility. On the other hand, the grinding of sodium chloride microcrystals to nanocrystals has not been reported so far, probably because it is difficult due to the necessity for the exclusion of water.

However, NaCl nanoparticles can be prepared by rapid evaporation of water from aerosols or by shock-cooling of NaCl vapour. Typically, such salt nanoparticles are studied with respect to their size-dependent deliquescence and efflorescence behaviour. For instance, Biskos *et al.* prepared NaCl nanoparticles with a size between 6 and 60 nm by an aerosol technique.[3] Lähde *et al.* prepared nanoscopic NaCl crystals with a diameter of 60–120 nm by spray-drying in the presence of leucine and lactose.[4] Park *et al.* prepared NaCl nanocrystals in a furnace reactor and also in an atomizer with particle sizes of 8 and 100 nm.[5] Earlier, we prepared metal halides, including NaCl, with a size of a few 100 nm by thermally-induced solid-state reaction from halogenoacetates and halogenopropionates.[6–8] The thermolysis of halogenobutyrates led to metal halide crystals with a diameter of a few µm.[9]

If sodium chloride nanocrystals are to be used as templates, *e.g.* for nanoporous polymers, they must be dispersable in organic solvents, *i.e.* their surface must be compatible with the hydrophobic solvent. Therefore, we used a classical organic reaction in which sodium chloride occurs as by-product.

Malonic ester syntheses represent a well established method in synthetic organic chemistry. Here, a carbanion is reacted with an alkyl halogenide to give C–C coupling under elimination of NaCl (Fig. 1).

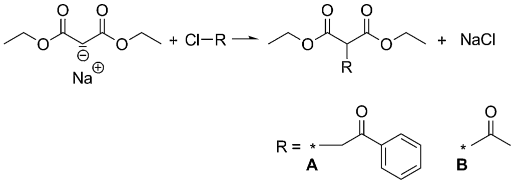

Fig. 1 The reaction of sodium diethylmalonate with phenacyl chloride (A) or acetyl chloride (B).

Of course, the organic reaction product is the focus of the synthesis, and the eliminated metal halide is usually ignored. We have carried out this synthesis with a special emphasis on the metal halide and found that it occurs as sub-micrometer crystals, an observation which was made as early as 1908 by Paal and Kühn.[10] This is interesting because this allows the facile preparation of NaCl nanocrystals which can be easily redispersed in organic solvents due to their generation in such a solvent. These nanocrystals may therefore serve as water-soluble nano-templates or porogens within polymeric or organic structures.

Materials and methods

X-Ray powder diffraction (XRD) was carried out with a Siemens D500 diffractometer (Cu-Kα radiation, $\lambda = 1.54$ Å) in Bragg–Brentano mode. Dynamic light scattering (DLS) of the colloidal dispersions was performed with a Malvern Zetasizer (Nano ZS, 633 nm laser; Smoluchowsky method). Scanning electron microscopy (SEM) was performed with a FEI Quanta 400 ESEM instrument after gold–palladium alloy sputtering. ATR-IR spectroscopy was carried out with a Varian 3100 FT-IR Excalibur Series Spectrometer equipped with a miRacle sample holder from PIKE.

Acetyl chloride (CH_3COCl; Fluka), phenacyl chloride (C_6H_5-CO-CH_2Cl; Fluka), diethyl malonate (Fluka), and sodium (Fluka) were all used in p.a. quality. All syntheses were carried out under strict exclusion of water, *i.e.* with thoroughly dried reagents and under inert gas atmosphere (argon).

Toluene was used in p.a. quality (J. T. Baker) and thoroughly dried over sodium. Dichloromethane was used in p.a. quality (Acros) and thoroughly dried over phosphorus pentoxide. Ethanol was used in p.a. quality (Sigma Aldrich) and thoroughly dried over sodium with the addition of 30 g L^{-1} of diethylphthalate.

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The syntheses were carried out as follows: 0.3 g sodium (13 mmol) were dissolved in 10 mL ethanol at room temperature. 2.08 g diethyl malonate (13 mmol) were added under stirring. 10 mL of toluene were added. 13 mmol of phenacyl chloride (dissolved in 20 mL toluene) or acetyl chloride (as pure liquid) were rapidly added under stirring at room temperature. The reaction immediately occurred as visible by the change of the colour of the reaction mixture from colourless to yellow/orange. Sodium chloride was isolated by centrifugation at 2500 g and washed with 20 mL ethanol. This was repeated until the NaCl was colourless (about five times). NaCl was then redispersed in dichloromethane for dynamic light scattering and scanning electron microscopy or dried in vacuum. A typical yield was 0.58 g (10 mmol; 76%) for phenacyl chloride and 0.7 g (12 mmol; 92%) for acetyl chloride.

For solvent-free syntheses, solid sodium diethyl malonate was isolated by removing the solvent ethanol in oil-pump vacuum. 2.37 g (13 mmol) of sodium diethyl malonate were reacted with 2.01 g (13 mmol) phenacyl chloride at room temperature after thorough mechanical mixing with a glass rod and storage at room temperature for 15 h. In the case of acetyl chloride, 2.37 g (13 mmol) of sodium diethyl malonate were cooled to −196 °C in a Schlenk tube under argon atmosphere. Then 1.2 g (15 mmol) of acetyl chloride (at room temperature) were added over 5 min with the Schlenk tube still immersed in liquid nitrogen. Then the Schlenk tube was taken out of the liquid nitrogen bath, and the initially solid mixture was allowed to warm up freely to room temperature over 20 min, thereby undergoing melting. If the reaction was carried out at room temperature, *i.e.* without pre-cooled diethyl malonate, the reaction was very vigorous (and would be potentially dangerous in an scaled-up process). The reaction mixtures were taken up in ethanol, and sodium chloride was isolated by centrifugation as described above.

Results and discussion

Fig. 2 shows the sodium chloride crystals that were obtained under different conditions with phenacyl chloride as chloride donor. If the reaction was carried out in toluene at room temperature, a uniform crystal population with a particle size of about 200 nm was obtained. The crystals were more or less spherical, but in some cases sharp edges occurred. If the reaction was carried out without solvent at room temperature, the particle size distribution was less uniform, but now crystals with a size between 100 and 300 nm were obtained. In this case, the initially solid reaction mixture rapidly liquefied and turned into a yellowish oil.

The particles were redispersed in dichloromethane (which was possible without ultrasonication), and the dispersions were studied by dynamic light scattering. Note that the sedimentation of NaCl (density 2.16 g cm^{-3}) was considerably slowed compared to an ethanolic dispersion by the higher density of CH_2Cl_2 (1.33 g cm^{-3}). The dispersions were stable for at least two weeks without visible sedimentation. Older dispersions with sedimented NaCl could be easily restored by shaking. Dynamic light scattering confirmed the disperse character of colloidal NaCl with an average particle size of 150–200 nm (Fig. 3). Equivalent results were obtained for the NaCl dispersions which resulted from solvent-free syntheses. The reason for this good dispersability is probably the adsorption of a thin layer of the organic reaction product on the NaCl surface. It is reasonable to assume that the phenyl groups are pointing towards the organic solvent.

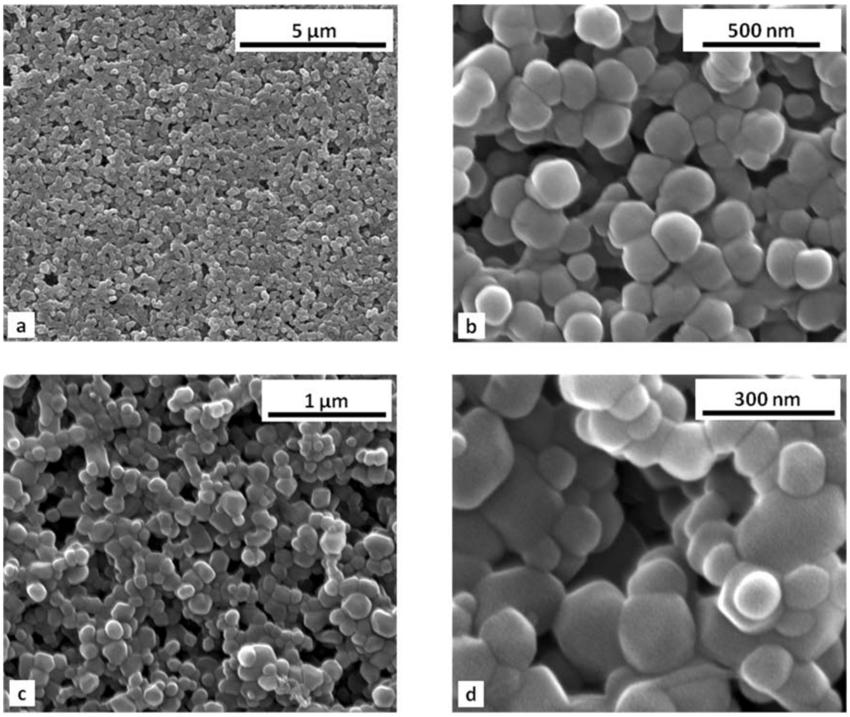

Fig. 2 Sodium chloride as product of the reaction between sodium diethylmalonate and phenacyl chloride in two different magnifications. The particle diameter was about 200 nm in both cases. (a) and (b): Reaction in toluene solution at room temperature. (c) and (d): Reaction without solvent at room temperature.

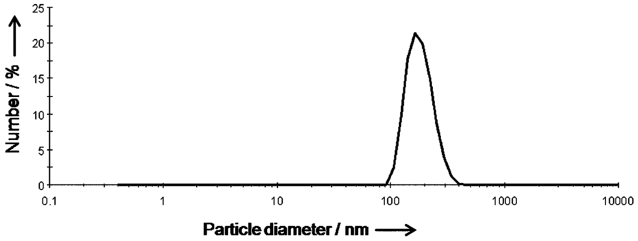

Fig. 3 Dynamic light scattering data of sodium chloride as product of the reaction between sodium diethylmalonate and phenacyl chloride, reacted in toluene, and redispersed in dichloromethane. The particle diameter was 190 nm (maximum by intensity) and 160 nm (maximum by number) (polydispersity index; PDI = 0.037).

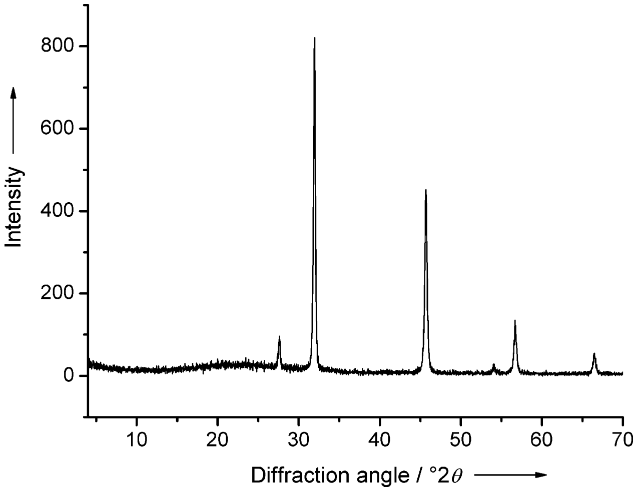

Fig. 4 X-Ray powder diffractogram of sodium chloride as product of the reaction between sodium diethylmalonate and phenacyl chloride in toluene. Only peaks of NaCl are visible.

The identity of the product NaCl was clearly shown by X-ray powder diffraction for syntheses in toluene as well as for solvent-free syntheses (Fig. 4).

The reaction was then transposed to acetyl chloride as a more reactive and liquid chlorine donor. If the reaction was carried out at room temperature in toluene, well-developed cubic crystals with a diameter of about 1–3 μm were obtained (Fig. 5). The reaction was vigorous, strongly exothermic and led to microcrystals. If the reaction was carried out without solvent, the sodium malonate had to be cooled to −196 °C to calm down the vigorous reaction (see Materials and methods for details). In this case, much smaller NaCl crystals with a diameter of 100–200 nm were obtained. However, the cubic shape of the crystals had almost vanished. X-Ray diffraction clearly showed the presence of NaCl (Fig. 6). In this case, dynamic light scattering of the dispersed NaCl crystals showed strongly agglomerated particles (μm-sized), *i.e.* a quantitative evaluation of the DLS data was impossible. In comparison to the organic product from phenacyl chloride, the product from acetyl chloride contains a methyl group instead of a phenyl group. This is not hydrophobic enough to turn to the organic solvent, and obviously the colloidal stabilization is not sufficient to prevent the agglomeration of the NaCl crystals.

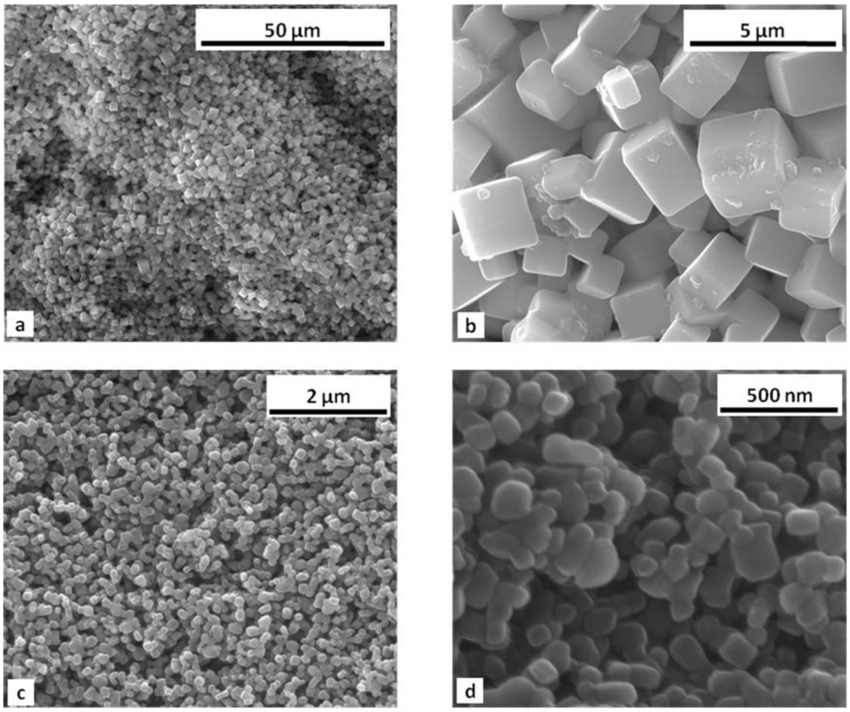

Fig. 5 Sodium chloride as product of the reaction between sodium diethylmalonate and acetyl chloride in two different magnifications. (a) and (b): The reaction in toluene solution at room temperature led to micrometer-sized crystals. (c) and (d): The reaction of the pure compounds at −196 °C led to agglomerated crystals with a diameter of about 100–200 nm.

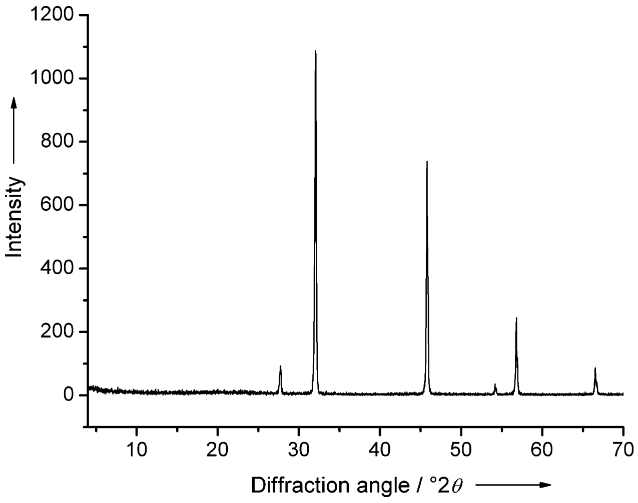

Fig. 6 X-ray powder diffractogram of sodium chloride as product of the reaction between sodium diethylmalonate and acetyl chloride in toluene at room temperature. Only peaks of NaCl are visible.

The NaCl crystals are covered by a thin layer of organic material as visible in the IR spectra (Fig. 7). The bands correspond to those expected for the malonic ester condensation products.

Conclusion

We found that the reaction between sodium diethyl malonate and phenacyl chloride or acetyl chloride, respectively, occurred rapidly in a vigorous, exothermic way, and led to the elimination of NaCl crystals. In solvent-free syntheses, smaller crystals were obtained, probably due to the higher rate of nucleation in the absence of a solvent. In contrast, the presence of a solvent led to a slower crystallization and to larger, cubically-shaped crystals. The particles can be easily separated from the organic reaction product, isolated and redispersed in organic solvents if phenacyl chloride is used as reagent, provided that all operations are carried out under strict exclusion of water. We assume that a thin layer of the organic product is coating the salt crystals, thereby acting like a surfactant and stabilizing the NaCl nanocrystals. To our knowledge, this is the first synthesis of uniform and dispersable sub-micrometre sodium chloride crystals. A potential application could be easily water-soluble nano-templates for polymeric or organic structures.

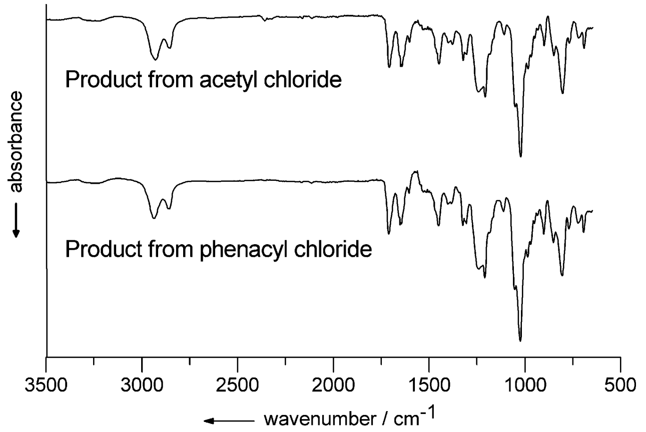

Fig. 7 Infrared spectra of NaCl crystals from the reaction of sodium diethylmalonate and acetyl chloride without solvent at –196 °C (top) and phenacyl chloride in toluene at room temperature (bottom), showing the bands of the organic condensation product.

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