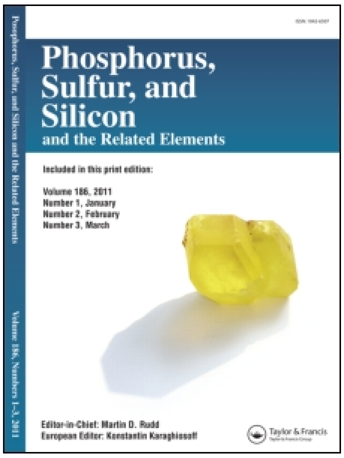

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DECOMPOSITION OF $P_2S_2N_4(Si(CH_3)_3)_4Al_2Cl_4$ AS STUDIED BY FT-RAMAN AND QUANTUM CHEMISTRY MEANS

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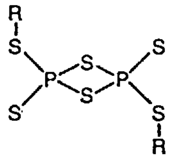
The dimeric title compound decomposes upon heating to give the monomer and desulphurized monomer as shown by FT-Raman and quantum chemical means.

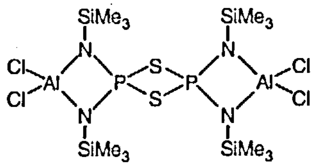
Keywords: $P_2S_2N_4(Si(CH_3)_3)_4Al_2Cl_4$; FT-Raman; quantum chemistry

INTRODUCTION

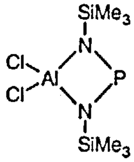
Davy compounds $[(RS)_2P_2S_4]$ (1) are important as thionation reagents in organic syntheses. It is assumed that the reaction mechanism for thionation of carbonyl groups for several Davy compounds involves the monomer $RSPS_2$, but little evidence for this intermediate has been given yet[1]. In fact, the monomer is predicted to be present in so small amounts that experimental proofs should be difficult to find.



(1)



(2)



(3)

The title compound (2) and its crystal structure were first described by Burford et al.[2] It has the same PS_2P ring as the Davy compounds and could therefore give clues to the reaction mechanism mentioned above.

EXPERIMENTAL/COMPUTATIONAL DETAILS

The Raman spectra were recorded with a Bruker Raman module FRA 106, attached to an IFS 66v spectrometer (Nd:YAG-laser: 1064 nm, 20-200 mW). For the calculations the 6-31G[3] basis augmented with polarization functions (*)[4] at HF/SCF level was used. The calculations were performed with the program GAMESS[5] on an Intel Paragon XPS.

RESULTS AND DISCUSSION

The title compound was investigated by FT-Raman both as solid at ambient temperature and as a melt at 180°C. Under melting the compound decomposed irreversibly to give a glassy compound after cooling.

To be able to interprete and assign the bands in the spectra, quantum chemical calculations including vibrational analysis of the title compound and its monomer were performed. In addition, calculations on the desulphurized monomer (3) were carried out, as the title compound is made by simply reacting (3) with sulphur[2].

Comparizons of structure[2] and calculated geometry, as well as of FT-Raman, FT-IR[6] and calculated spectra of the title compound show that there is a good fit between the experimental and theoretical results - taking into account that the calculations represent a single gas-phase molecule, and not a crystal. Scaling factors range from ca 0.9 for methyl and P-S vibrations and up to 0.97 for some skeleton stretching modes.

The energy calculations indicate that the title compound and its monomer have almost the same thermodynamic stability. In fact, the monomer is slightly favoured according to the HF/SCF calculations; but this level tends to underestimate dimerization energies. The low dimerization energy could nevertheless explain why the decomposition seems to be irreversible.

For the dimer, the four frequencies mainly belonging to P-S stretching vibrations were calculated to 695, 414 (both IR active), 500 and 432 (both

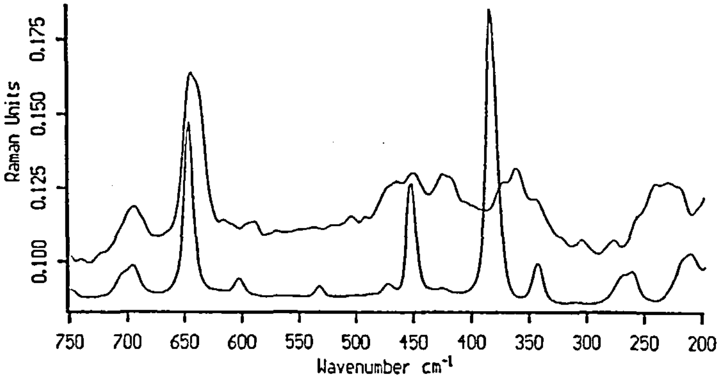


FIGURE 1 FT-Raman spectra of the title compound at 20°C (lower) and of the melt at 180°C (upper spectrum)

Raman active) cm^{-1}. Experimentally, the main bands are found at 616.6 and 378.1 cm^{-1} [2,6] in the IR spectrum and at 453 and 384 cm^{-1} in the Raman spectrum. The scaling factors of 0.89-0.91 agree with previously found scaling factors of about 0.90 for the stretches in the PS_2P ring of $P_2S_6^{2-}$ [7].

The monomer gives rise to many more bands in the Raman spectrum as all vibrations are active in the C_{2v} symmetry. Comparizon of the Raman spectra shows clearly that the PS_2P ring is broken under heating. The P-S stretch band at 384 cm^{-1} disappears completely, while the band at 453 cm^{-1} disappears and is replaced by or reveals a weak band at 450 cm^{-1}.

The P-S stretch of the monomer is found at 637 cm^{-1}, while the out-of-plane bend appears at 416 cm^{-1}. According to the calculations, no bands should be found in the region 410-350 cm^{-1}, if only the monomer was present in the melt. But here one finds two distinct bands at 374 and 361 cm^{-1}. The calculations reveal that these belong to the desulphurized monomer (3). On the other hand, (3) has no bands in the region 510-380 cm^{-1}, while monomer bands at 504, ~465, and 416 cm^{-1} are found here. Hence, both compounds must be present in the melt.

Additionally the bands of the monomer and (3), there are bands at 474, 450, and 257(shoulder) cm^{-1} in the spectrum of the melt. Together with the bands at 242, 218, 150, and 84 cm^{-1}, these can be assigned to sulphur as S_8 and S_6[8].

The presence of sulphur in the solid is uncertain as the most prominent sulphur bands coincide with bands from the dimer (2). The band at 425/426 cm^{-1}, which appears with same intensity for both the solid and the melt, is probably due to an as yet unidentified impurity.

CONCLUSION

The study indicates that (2) upon melting breakes down to a mixture of the monomer and (3). The presence of the monomer indicates that a dimer/ monomer equilibrium may be present also for the Davy compounds, and therefore, that the Davy monomer may be the active agent in thionation reactions.

Acknowlegdements

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