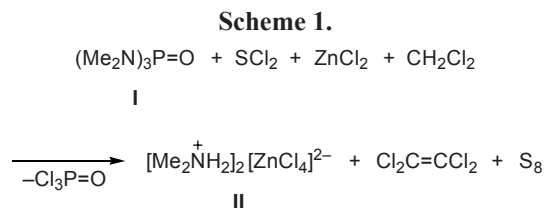


SHORT
COMMUNICATIONSReaction of the System Sulfur(II) Chloride–Zinc(II) Chloride
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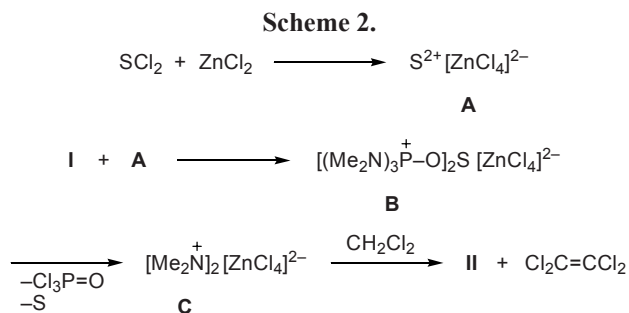
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Normant [1] reported on the reaction of hexamethylphosphoramide (**I**, HMPA) with hydrogen chloride, which involved protonation of one amino group and its subsequent elimination as dimethylamine. We were the first to reveal that hexamethylphosphoramide reacts with sulfur(II) chloride in the presence of zinc(II) chloride in methylene chloride to give ammonium salt **II** with participation of solvent molecule (Scheme 1).



Presumably, the process includes a number of steps, the first of which is transformation of sulfur(II) chloride into electrophilic species **A**. The reaction of **A** with HMPA produces phosphonium ion **B** which is responsible for generation of cation **C**. The latter reacts with methylene chloride acting as hydrogen donor, thus completing the formation of dimethylammonium

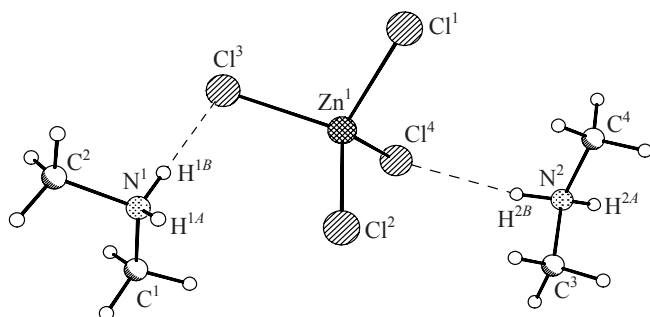


tetrachlorozincate (**II**). Intermediate species generated during this process give rise to tetrachloroethylene. The final product of the transformation of HMPA is mainly phosphoryl chloride (Scheme 2).

The structure of salt **II** was determined by X-ray analysis (see figure) and ¹H NMR data. Monoclinic crystals, C₄H₁₆Cl₄N₂Zn, with the following unit cell parameters [at 100(2) K]: *a* = 8.3760(5), *b* = 11.3953(7), *c* = 13.0976(8) Å; β = 90.091(1)°; *V* = 1250.13(13) Å³; *Z* = 4; space group *P*2(1)/*n*; *d*_{calc} = 1.591 g/cm³; μ = 2.773 mm⁻¹. Total of 9206 reflections were measured, 3345 of which were independent (*R*_{int} = 0.0182); *R* = 0.0195 [for reflections with *I* > 2σ(*I*)], *wR*₂ = 0.0486 (for all reflections). The crystalline structure of compound **II** is characterized by hydrogen bonds Cl⋯H [2.33(2)–2.48(2) Å] that are considerably shorter than shortened Cl⋯H contacts (2.67 Å) [2].

Single crystals of compound **II** were grown from a solution in acetonitrile according to the procedure described in [3]. Tetrachloroethylene was identified by gas–liquid chromatography.

Dimethylammonium tetrachlorozincate (II). The reaction was performed under conditions excluding contact with atmospheric moisture. A solution of 1.621 g (15.7 mmol) of sulfur(II) chloride in 5 ml of methylene chloride was added dropwise to a mixture of 2.14 g (15.7 mmol) of zinc(II) chloride and 10 ml of methylene chloride under stirring at –15°C. A solution of 5.6 g (31 mmol) of HMPA in 5 ml of methylene chloride was then added, and the mixture was allowed to warm up to room temperature and stirred for 1 h. The precipitate was filtered off and recrystallized from acetonitrile. Yield 2.18 g (53%), colorless powder,



Structure of the molecule of dimethylammonium tetrachlorozincate (**II**) according to the X-ray diffraction data.

mp 124–126°C (decomp.). ^1H NMR spectrum, δ , ppm: 2.72 s (3H, CH_3), 2.66 s (3H, CH_3). Found, %: C 16.32; H 5.54; Cl 47.65; N 9.03; Zn 21.46. $\text{C}_4\text{H}_{16}\text{Cl}_4\text{N}_2\text{Zn}$. Calculated, %: C 16.05; H 5.35; Cl 47.49; N 9.37; Zn 21.74. The filtrate was evaporated under reduced pressure. According to the IR data, the residue contained mainly phosphoryl chloride. IR spectrum, ν , cm^{-1} : 1295 (P=O), 550 (P–Cl).

The ^1H NMR spectra were recorded on a Bruker DPX 200 spectrometer at 200 MHz using $\text{DMSO-}d_6$ as solvent and tetramethylsilane as internal reference. The IR spectra were measured on a Perkin–Elmer 180 instrument from samples prepared as thin films. The purity of compound **II** was checked by TLC on Silufol UV-254 plates or Silpearl silica gel (hexane–diethyl ether, 10:1); development with iodine vapor. GLC

analysis was performed on a Tsvet-110 chromatograph equipped with a flame ionization detector and a 3-m \times 3-mm column packed with 15% of Carbowax 6000 on Chromaton N-AW; oven temperature 80°C, injector temperature 150°C; carrier gas N_2 , flow rate 2 l/h).

A set of experimental reflection intensities was acquired on a Smart APEX automatic diffractometer (graphite monochromator, MoK_α irradiation, ω – θ scanning; $2.37 \leq \theta \leq 29.15^\circ$). The structure was solved by the direct method and was refined with respect to F_{hkl}^2 by the least squares procedure in anisotropic approximation for all non-hydrogen atoms. The positions of hydrogen atoms were determined by the Fourier difference synthesis and were refined isotropically. All calculations were performed using SHELXTL V. 6.10 [4].

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