Nitrosonium hexachlorostannate: synthesis, crystal structure, and nitrosating activity in the reactions with arylcyclopropanes

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Nitrosonium hexachlorostannate $(NO)_2[SnCl_6]$ was synthesized by the reaction of NOCl and $SnCl_4$ in CH_2Cl_2. According to the single-crystal X-ray diffraction analysis data, the structure of $(NO)_2[SnCl_6]$ consists of cations NO^+ and octahedral anions $[SnCl_6]^{2-}$ arranged as ions in antifluorite. Isoxazolines were synthesized by the reactions of $(NO)_2[SnCl_6]$ with arylcyclopropanes containing donor substituents in the aromatic ring.

Key words: nitrosonium hexachlorostannate, arylcyclopropanes, nitrosation, isoxazolines, X-ray diffraction analysis.

Interest in nitrosating agents is due to a great extent to their possible use in syntheses of various nitrogen-containing heterocycles. In particular, the nitrosation of cyclopropanes affords isoxazole and isoxazoline derivatives.[1] In previous works, $NO[BF_4]$ (see Ref. 2) or nitrosyl chloride[3] activated with sulfur(IV) and sulfur(VI) oxides[3] were used for nitrosation of cyclopropanes. It should be mentioned that polarity of the NO—A bond of the reactant (where A = Cl^-, $[BF_4]^-$) substantially affects the nitrosation rate, and compounds with ionic bond are most promising. In addition, the possibility of occurrence of any side reactions accompanying nitrosylation reactions is determined, to a considerable extent, by the nature of residue A (see Refs 3 and 4). Therefore, search for new nitrosonium salts and investigation of their nitrosating ability are very urgent.

Nitrosonium hexachlorostannate is a representative of the well known family of nitrosonium chlorometallates $(NO)_2[MCl_6]$ (M = Ti, Sn, V).[5,6] Nevertheless, its crystal structure remained unstudied until presently. In this work, we improved the method for the synthesis of $(NO)_2[SnCl_6]$, pioneered in testing its nitrosating activity towards arylcyclopropanes and investigated its crystal structure by single-crystal X-ray diffraction analysis.

Nitrosonium hexachlorostannate was synthesized by the reaction of NOCl and $SnCl_4$ in CH_2Cl_2. The use of more volatile solvent instead of usually used CCl_4 (see Refs 6 and 7) (boiling points of CH_2Cl_2 and CCl_4 are 40 and 75.6 °C, respectively[8]) made it possible to remove solvent under reduced pressure (~10 Torr) instead of usually used filtration to remove crystals that formed. As a result, the design of the apparatus was simplified and the yield and purity of the product were enhanced, because the contact of the reaction mixture with air moisture was completely excluded during the whole synthesis. The obtained sample of $(NO)_2[SnCl_6]$ was a light yellow powder unstable in air and vigorously decomposing in water to evolve nitrogen oxides. The single-phase character of $(NO)_2[SnCl_6]$ was confirmed by X-ray diffraction analysis.

According to the single-crystal X-ray structure analysis data, the crystal structure of $(NO)_2[SnCl_6]$ is formed by anions $[SnCl_6]^{2-}$ and cations NO^+. The packing of the cations and complex anions in $(NO)_2[SnCl_6]$ corresponds to the antifluorite structure (Fig. 1). The octahedral anions with the local symmetry C_4 have a slight tetragonal distortion: the Sn—Cl bonds in the equatorial plane are somewhat shorter than those on the axial axis parallel to the crystallographic axis *c*, being 2.418(3) and 2.435(5) Å, respectively. Each anion is surrounded by eight cations NO^+, whose "centers of gravity" are localized in the vertices of a weakly distorted cube, and the oxygen and nitrogen atoms are randomly disordered both between each other and over two different positions. The same disordering type of cations NO^+ was observed in high-temperature modifications of nitrosonium hexachlorometallates $(NO)_2[TiCl_6]$ (see Ref. 5) and $(NO)_2[VCl_6]$ (see Ref. 6) isostructural to $(NO)_2[SnCl_6]$.

Each NO^+ cation is surrounded by four $[SnCl_6]^{2-}$ anions. The lengths of contacts of the nitrogen and oxygen atoms with the eight nearest chlorine atoms range from 2.94 to 3.27 Å, whereas the N—Cl bond in crystalline NOCl is substantially shorter,[9] being 2.19 Å. Thus, the NO^+ cation in the structure of $(NO)_2[SnCl_6]$ forms bonds of ionic nature with the chlorine atoms.

Among the hexachlorostannates described, only one polymorphous modification of $K_2[SnCl_6]$, which is stable

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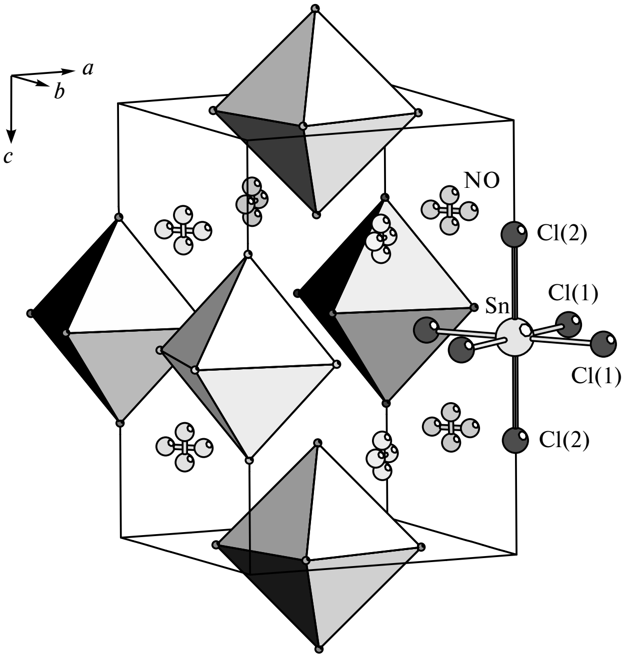


Fig. 1. Fragment of the crystal structure of $(NO)_2[SnCl_6]$. Four O(N) atoms with population 0.25 each are bound by the local inversion center and correspond to the cation NO^+ owing to disordering.

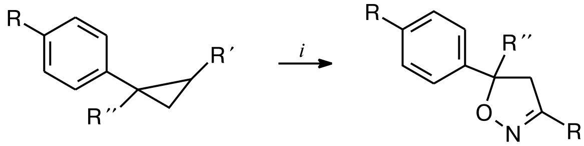
in the temperature range from 255 K to room temperature, crystallizes in the same space group $P4/mnc$ as $(NO)_2[SnCl_6]$ (see Ref. 10). Proximity in crystal structures and similarity of unit cell parameters of $K_2[SnCl_6]$ and $(NO)_2[SnCl_6]$ (unit cell volumes V = 497 and 492 Å^3, respectively) indicate that the effective sizes of the K^+ and NO^+ cations are close, which confirms the ionic character of the bond between the cations NO^+ and anions $[SnCl_6]^{2-}$.

Unlike the nitrosonium derivatives, other hexachlorostannates M_2SnCl_6 (M = K, Rb, Cs, NH_4, Tl) at room temperature crystallize in the cubic crystal system (space group Fm-3m, structural type of K_2PtCl_6) with the antifluorite-type arrangement of cations M^+ and ideal octahedral anions $[SnCl_6]^{2-}$ (see Ref. 11). An extended rather than spherical shape of the NO^+ cation can be a reason for a slight distortion of the octahedral anions in nitrosonium hexachlorometallates $(NO)_2[MCl_6]$ (M = Sn, Ti, V) and for non-coinciding turn angles of these anions about the axis C_4.[5,6]

As the temperature decreases, nitrosonium hexachlorometallates $(NO)_2[MCl_6]$ (M = Sn, Ti, V) undergo a phase transition to the monoclinic crystal system (space group $P2_1/n$). According to the literature data,[6] the phase transition temperature for $(NO)_2[SnCl_6]$ is 231 K, which substantially exceeds the temperature of a single-crystal X-ray structure determination experiment (100 K). No phase transition was observed during the single-crystal X-ray experiment. This can be explained, most likely, by the fact that a single crystal was cooled to the temperature much lower than the phase transition temperature within 1—2 s, while at the temperature of the single-crystal X-ray experiment no phase transition occurred for kinetic reasons.

The ionic character of the bond between the nitrosonium cation and the anion in crystalline $(NO)_2[SnCl_6]$ suggests that it can be a promising nitrosating agent for organic synthesis. The nitrosating ability of $(NO)_2[SnCl_6]$ was studied in the reactions with a series of substituted arylcyclopropanes **1a—f** affording substituted 5-arylisoxazolines **2a—f** in high yields (Scheme 1).

Scheme 1



1a—f **2a—f**

Compound	R	R′	R″	Yield (%)
2a	MeO	H	H	60
2b	Me	H	H	99
2c	H	H	H	75
2d	MeO	Ph	H	82
2e	MeO	4-MeOC$_6$H$_4$	H	78
2f	H	H	Me	80

i. $(NO)_2[SnCl_6]$, CH_2Cl_2, −20—0 °C, 15 min—3 h.

The reactions were carried out in CH_2Cl_2 with high dilution of the reactants, the optimal temperature being –20—0 °C. The reaction rate decreases noticeably at lower temperatures; however, at 20 °C a considerable amount of 4-methoxycinnamaldehyde is formed in the case, *e.g.*, of cyclopropane **1a**.[12]

The quantitative conversion of arylcyclopropanes is achieved already at the ratio substrate : reactant = 2 : 1, *i.e.*, the both nitrosonium cations of the reactant are involved in nitrosation.

Thus, in this work we determined the crystal structure of nitrosonium hexachlorostannate by single-crystal X-ray diffraction analysis and proved the ionic character of the bond between the nitrosonium cation NO^+ and anion $[SnCl_6]^{2-}$. The study of the reactivity of nitrosonium hexachlorostannate in the reactions with cyclopropanes showed that it is a mild nitrosating agent and can successfully be used for the synthesis of isoxazolines from arylcyclopropanes containing electron-donor substituents in the aromatic ring. Among doubtless advantages of $(NO)_2[SnCl_6]$ as nitrosating agent is its convenient storage and relative availability compared to $NO[BF_4]$.

Experimental

The following reagents were used in the synthesis of $(NO)_2[SnCl_6]$: $NaNO_2$ (reagent grade), $SnCl_4$ (reagent grade), PCl_5 (reagent grade), P_2O_5 (reagent grade), CCl_4 (reagent grade), and CH_2Cl_2 (reagent grade) distilled over P_2O_5. The ^1H NMR spectra of the isoxazolines ($CDCl_3$) were recorded on Varian XR-400 and Bruker Avance-400 spectrometers with a working frequency of 400 MHz (hexamethyldisiloxane was used as an internal standard).

The starting arylcyclopropanes were synthesized by reduction of the corresponding 1-aryl-2,2-dichlorocyclopropanes[13] or decomposition of the corresponding pyrazolines.[14] Phosphorus oxotrichloride $POCl_3$ was synthesized using the known procedure[7] by the reaction of P_2O_5 with PCl_5.

Nitrosonium hexachlorostannate was synthesized from NOCl and $SnCl_4$ under the conditions excluding contact of the reactants with air moisture. The controlled current of gaseous NOCl was provided by heating a mixture of $NaNO_2$ and $POCl_3$ according to the described procedure.[7] Formed NOCl was fed into a reactor cooled to 0 °C and containing a solution of tin tetrachloride (5 mL) in dichloromethane (10 mL) with continuous magnetic stirring. During the reaction the solution became turbid because of $(NO)_2[SnCl_6]$ precipitation. The reaction time was 1 h and the overall amount of gaseous NOCl passed through the reactor within this time corresponded to the mole ratio $NOCl : SnCl_4 = 4 : 1$. After the end of the reaction, the solvent was distilled off *in vacuo*. The yield was ~96%.

Isoxazolines 2a—f (general procedure). Arylcyclopropane **1** (1.0 mmol) in CH_2Cl_2 (5 mL) was added with stirring to a suspension of $(NO)_2[SnCl_6]$ (0.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After the end of the reaction (the reaction course was monitored by TLC), the reaction mixture was neutralized with a solution of Na_2CO_3 and washed with water. Aqueous layers were extracted with dichloromethane (3×10 mL) and the combined extracts were dried with Na_2SO_4. The solvent was evaporated and the products were isolated by chromatography or recrystallization and characterized spectrally by comparing with the literature data.[2,3,12,15]

X-ray diffraction phase analysis was carried out on a DRON-3 diffractometer (Cu-Kα radiation, graphite monochromator). A sample was prepared in a dry box and covered with polystyrene film to protect from moisture. The X-ray pattern obtained corresponded completely to the theoretical one calculated for $(NO)_2[SnCl_6]$ on the basis of the single-crystal X-ray structure analysis results.

Single-crystal X-ray diffraction analysis. Single crystals of $(NO)_2[SnCl_6]$ with sizes suitable for single-crystal X-ray analysis were obtained by the recrystallization of a small amount of finely crystalline sample in a sealed glass ampule from a hot solution in CCl_4 (80 °C) with gradual cooling to room temperature for 24 h. To protect from air moisture, single crystals of $(NO)_2[SnCl_6]$ were sampled under a Nujol layer using a polarization microscope. Single-crystal X-ray diffraction analysis was carried out on an IPDS2 instrument (STOE) (Mo-Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 100±2 K. The structure of $(NO)_2[SnCl_6]$ was solved by direct method and refined in the anisotropic approximation for all atoms. The cation NO^+ is disordered over two positions with additional disordering between the O and N atoms. The crystallographic data, main characteristics of diffraction experiment, and refinement parameters for the structure of $(NO)_2[SnCl_6]$ are presented in Table 1. The crystallographic data were deposited with the Inorganic Crystal Structure Database, FIZ Karlsruhe and NIST, Gaithersburg, No. 421 052.

Table 1. Crystallographic characteristics, the diffraction experimental details, and refinement parameters for the structure of $(NO)_2[SnCl_6]$

Parameter	Value
Molecular formula	$Cl_6N_2O_2Sn$
Molecular weight	391.44
Crystal system	Tetragonal
Space group	*P*4/*mnc*
a/Å	6.922(1)
c/Å	10.267(2)
V/Å^3	491.9(1)
Z	2
d_{calc}/g cm^{-3}	2.642
μ/mm^{-1}	4.180
Crystal size/mm	0.2×0.2×0.2
T/K	100(2)
θ_{max}/deg	28.4
Number of measured/independent reflections	3500/330
Number of reflections with $F^2 > 2\sigma(F^2)$	326
Number of refined reflections/parameters	330/22
R_1/wR_2	0.0535/0.1411

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References

1. G. Desimony, G. Faita, *Seminars in Organic Synthesis*, *16th Summer School "A. Corbella," (Milan, June 17—21, 1991)*, Milan, 1991, p. 4.1.
2. K. Mizuno, N. Ichinose, T. Tamai, Y. Otsuji, *J. Org. Chem.*, 1992, **57**, 4669.
3. O. B. Bondarenko, A. Yu. Gavrilova, L. G. Saginova, N. V. Zyk, N. S. Zefirov, *Zh. Org. Khim.*, 2009, **45**, 230 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2009, **45**, 218].
4. V. N. Tikhanushkina, Ph. D. (Chem.) Thesis, Moscow Pedagogical State University, Moscow, 2007 (in Russian).
5. H. Henke, *Z. Kristallogr.*, 2002, **217**, 474.
6. H. Henke, *Z. Kristallogr.*, 2003, **218**, 617.
7. *Praktikum po neorganicheskoi khimii* [*Practical Works on Inorganic Chemistry*], Ed. Yu. D. Tret´yakov, Akademiya, Moscow, 2004, 384 pp. (in Russian).
8. *Svoistva organicheskikh soedinenii* [*Properties of Organic Compounds*], Ed. A. A. Potekhin, Khimiya, Leningrad, 1984, 518 pp. (in Russian).
9. A. Ellern, K. Seppelt, *Z. Anorg. Allg. Chem.*, 2001, **627**, 234.
10. H. Boysen, A. W. Hewat, *Acta Crystallogr.*, *Sect. B: Struct. Sci.*, 1978, **34**, 1412.
11. *Inorganic Crystal Structure Database*, *FIZ Karlsruhe and NIST*, Gaithersburg; http://www.fiz-karlsruhe.de/icsd.html.

12. O. B. Bondarenko, A. Yu. Gavrilova, M. A. Kazantseva, V. N. Tikhanushkina, E. E. Nifant´ev, L. G. Saginova, N. V. Zyk, *Zh. Org. Khim.*, 2007, **43**, 566 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2007, **43**, 564].
13. S. S. Mochalov, D. V. Kosynkin, I. D. Yudin, K. A. Zavodskikh, Yu. S. Shabarov, N. S. Zefirov, *Khim. Geterotsikl. Soedin.*, 1994, **30**, 472 [*Chim. Heterocycl. Compd.* (*Engl. Transl.*), 1994, **30**].
14. A. Kost, V. V. Ershov, *Zh. Org. Khim.*, 1957, **11**, 3874 [*Russ. J. Org. Chem.*, 1957, **11**].
15. L. G. Saginova, I. L. Kukhareva, A. T. Lebedev, Yu. S. Shabarov, *Zh. Org. Khim.*, 1991, **27**, 1852 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1991, **27**].

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