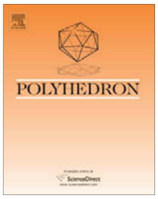
Polyhedron 29 (2010) 991–994

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



A new route to the syntheses of N-(fluorosulfuryl)sulfonamide salts: Crystal structure of Ph_4P^+ $[CF_3SO_2NSO_2F]^-$

Martin Beran [a], Jiří Příhoda [b,*], Jan Taraba [c]

[a] *Institute of Analytical Chemistry of ASCR, v.v.i., Veveří 97, 602 00 Brno, Czech Republic*
[b] *Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
[c] *Episcopical High School, Barvičova 85, 602 00 Brno, Czech Republic*

ARTICLE INFO

Article history:
Received 4 August 2009
Accepted 30 November 2009
Available online 21 December 2009

Keywords:
N-(fluorosulfuryl) sulfonamides
N-(fluorosulfuryl)trifluoromethane sulfonamide
N-(chlorosulfuryl)trifluoromethane sulfonamide

ABSTRACT

A new route for the preparation of potassium and tetraphenylphosphonium salts of N-(fluorosulfuryl)trifluoromethane sulfonamide is described. N-(chlorosulfuryl)-trifluoromethane sulfonamide CF_3SO_2–NH–SO_2Cl, that was used for preparations of both salts, was prepared by the reaction of trifluoromethane sulfonamide $CF_3SO_2NH_2$ and chlorosulfonic acid in the presence of $SOCl_2$. The obtained N-(chlorosulfuryl)trifluoromethane sulfonamide was converted to potassium N-(fluorosulfuryl)trifluoromethane sulfonamide by using anhydrous KF. Potassium N-(fluorosulfuryl)trifluoromethane sulfonamide served as a starting material for the preparation of the corresponding tetraphenylphosphonium N-(fluorosulfuryl)trifluoromethane sulfonamide that crystallizes from the aqueous solution of potassium N-(fluorosulfuryl)trifluoromethane sulfonamide and tetraphenylphosphonium chloride. N-(fluorosulfuryl)trifluoromethane sulfonamide tetraphenylphosphonium salt is tetragonal, space group $P\bar{4}$.

1. Introduction

Salts of N-(fluorosulfuryl) sulfonamide of the general formula $RSO_2N^{(-)}SO_2F$ are structurally similar to the salts of imido-bis(sulfuric) acid difluoride, $(FSO_2)_2N^-$. Therefore similar physico-chemical properties of both classes of these compounds can be expected. Simple synthesis of potassium and lithium bis(fluorosulfuryl) imides was published earlier [1,2] and both compounds belong to industrially very interesting and perspective materials. These salts have found their utilization as constituents of electrolytes in lithium batteries and therefore similar exploitation in the case of N-(fluorosulfuryl) sulfonamide salts can be expected. Other N-(fluorosulfuryl) sulfonamide salts were only rarely studied and the only suitable synthesis of CF_3SO_2–NH–SO_2F and its silver salt was published in [3].

The preparation of CF_3SO_2–NH–SO_2F consisted of the reaction of $CF_3SO_2N{=}PCl_3$ with HSO_3F with a yield of approx. 90%. CF_3SO_2–NH–SO_2F was isolated by fraction distillation from the reaction mixture and was converted into Ag-salt by the reaction with silver oxide in benzene. However, this synthetic route is, in fact, apparently more complex as shown by Taraba et al. [4]. In their attempts to prepare CF_3SO_2–NH–SO_2F they proved that the reaction between $CF_3SO_2N{=}PCl_3$ with HSO_3F leads predominantly to the formation of CF_3SO_2–NH–SO_2–NH–SO_2CF_3 whereas the expected CF_3SO_2–NH–SO_2F was present only in negligible amounts in the reaction mixture. We also tried to prepare CF_3SO_2–NH–SO_2F in a similar way but the product CF_3SO_2–NH–SO_2F contained residual $POCl_3$ that could not be removed by fraction distillation (proved by ^{31}P NMR spectroscopy). Therefore this product cannot be used for the preparation of the salts, and another route had to be found out.

Recently, we studied the reaction between amidosulfuric, HSO_3NH_2, and chlorosulfuric, HSO_3Cl, acids in thionyl chloride [1]. The main product of this reaction was imido-bis(sulfuric)acid dichloride, $(ClSO_2)_2NH$, that was formed easily and almost in quantitative yield. This led us to the idea that the reaction of similar compounds, e.g. alkyl sulfonamide with chlorosulfuric acid, could lead to the formation of the corresponding N-(chlorosulfuryl)alkyl sulfonamides. Suggested course of the reaction between trifluoromethane sulfonamide (**1**) with chlorosulfuric acid, HSO_3Cl, in thionyl chloride is shown in Scheme 1.

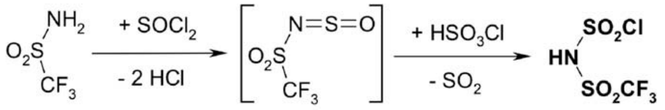
The compound (**2**) is intended to be used for preparations of N-(fluorosulfuryl)trifluoromethane sulfonamides by simple conversion with the corresponding fluorides.

This article deals with a new route to the synthesis of N-(chlorosulfuryl)trifluoromethane sulfonamide (**2**) and potassium (**3**) and tetraphenylphosphonium (**4**) salts of N-(fluorosulfuryl)trifluoromethane sulfonamide. The compound (**4**) is the first substance in which the structure of N-(fluorosulfuryl)trifluoromethane sulfonamide anion was determined by X-ray diffraction.

---

[*] Corresponding author. Tel.: +420 549496690; fax: +420 549492443.
E-mail address: prihoda@chemi.muni.cz (J. Příhoda).

0277-5387/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2009.11.024



1 2

Scheme 1. Suggested course of N-(chlorosulfuryl)trifluoromethane sulfonamide (**2**) synthesis.

2. Results and discussion

*2.1. N-(chlorosulfuryl)trifluoromethane sulfonamide (**2**)*

The reaction between trifluoromethane sulfonamide (**1**) and HSO_3Cl in $SOCl_2$ led to the formation of a hygroscopic compound which yielded a white solid (69%) after recrystallization from CCl_4. When exposed to air fumes are evolved due to the hydrolysis and formation of gaseous HCl. Only one dominant resonance signal at -75.49 ppm can be found in ^{19}F NMR spectrum. Other resonance signals are negligible which indicates high fluorine purity of the compound (**2**).

*2.2. Potassium N-(fluorosulfuryl)trifluoromethane sulfonamide (**3**)*

The conversion of (**2**) to (**3**) by using potassium fluoride can be carried out with the crude product, i.e. without preliminary recrystallization described above. The conversion process leading to potassium N-(fluorosulfuryl)trifluoromethane sulfonamide (**3**) was carried out by heating the mixture of the crude (**2**) with anhydrous KF in absence of a solvent at 170 °C (similar approach was used for converting of imido-bis(sulfuric)acid dichloride into potassium bis(fluorosulfuryl) imide [1]) – Scheme 2.

The yield of potassium N-(fluorosulfuryl)trifluoromethane sulfonamide (**3**) was 84% (related to trifluoromethane sulfonamide). This substance was characterized by ^{19}F NMR spectroscopy. There are two main resonance signals in ^{19}F NMR spectrum (in THF) – a quartet ($\delta = 55.6$ ppm, $J_{FF} = 5$ Hz, relative intensity 33.6, $-SO_2F$) and a doublet ($\delta = -79.6$ ppm, $J_{FF} = 5$ Hz, relative intensity 97.2, $-SO_2CF_3$). A negligible signal belongs apparently to fluorine atoms of bis(fluorosulfuryl) imide anion ($\delta = 51.3$ ppm, relative intensity 1). The fluorine spectrum of potassium N-(fluorosulfuryl)trifluoromethane sulfonamide (**3**) is in agreement with the suggested structure and is very well comparable to the published ^{19}F NMR spectra of free N-(fluorosulfuryl)trifluoromethane sulfonamide (doublet -77.7 ppm, quartet 58.5 ppm, $J_{FF} = 2.9$ Hz) and its silver salt (doublet -79.3 ppm, quartet 56.2 ppm, $J_{FF} = 3.4$ Hz) [3].

The compound (**3**) was characterized by Raman spectroscopy. An attempt to assign some basic vibrations was done on the basis of analogy with spectra of alkali metal bis(fluorosulfuryl) imides [2], ammonium bis(fluorosulfuryl) imide [5], and $FXeN(SO_2F)_2$ [6].

The dominating band at 743 cm^{-1} was assigned to the valence vibration ν_sSNS. This wavelength is almost consistent with the position of the corresponding band of potassium bis(fluorosulfuryl) imide (749 cm^{-1}). Valence vibration νSF corresponds to the band at 858 cm^{-1}, vibrations $\nu_s SO_2$ and $\nu_{as} SO_2$ to the bands at 1237 cm^{-1} and 1325–1362 cm^{-1}, respectively. The band belonging $\nu_s CF_3$ can be expected in the region around 1100 cm^{-1} but was not observed.

*2.3. Tetraphenylphosphonium N-(fluorosulfuryl)trifluoromethane sulfonamide (**4**)*

Since attempts at crystal growth of (**3**) were not successful X-ray structure determinations could not be carried out. However, another salt containing the same anion could be prepared. Well crystallizing tetraphenylphosphonium salt (**4**) was prepared by precipitating of (**3**) with tetraphenylphosphonium chloride in aqueous solution (Scheme 3). The pure product was isolated by extraction into CH_2Cl_2.

The compound (**4**) was fully characterized by X-ray structural analysis and it can be assumed that the structure of the anion in potassium salt (**3**) is expected to achieve very similar geometry. The structure of N-(fluorosulfuryl)trifluoromethane sulfonamide anion in (**4**) is the first known structure of this compound type.

*2.4. Crystal structure of tetraphenylphosphonium N-(fluorosulfuryl)trifluoromethane sulfonamide (**4**)*

The substance (**4**) crystallizes in tetragonal space group $P\bar{4}$. All details describing its structure follow from Table 1 and Fig. 1.

Comparison of basic bond lengths and angles to the equivalent data of similar salts of imido-bis(sulfuric acid) difluoride is shown in Table 2.

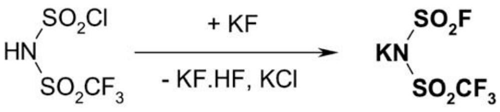
It follows from Table 2 that the corresponding bond lengths both in **(4)** and other bis(fluorosulfuryl) imides are comparable in most cases. Rather longer is the S1–O1 bond; the bond length is 1.484 Å in **(4)** while lengths of the same bond in bis(fluorosulfuryl) imides are in the interval 1.378–1.423 Å. On the other hand, the bond S1–N1 (in (**4**) is 1.529 Å) is shorter as compared to other S–N bonds in bis(fluorosulfuryl) imides (1.556–1.642 Å). This means that the S1–N1 bond in (**4**) has higher bond order. The SNS angle in all compared substances is practically identical (123–124°) with the only exception of $CsN(SO_2F)_2$ (120.8°).

3. Experimental

All reactions except preparation of the Ph_4P salt were performed under nitrogen and anhydrous conditions using conventional Schlenk techniques.

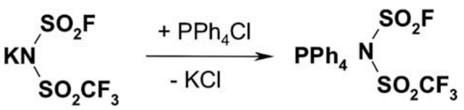
Solvents were supplied by Lachema and dried by conventional methods prior to use. Thionyl dichloride was supplied by Web Laborchemie Apolda and distilled with quinoline and linen oil before use. Potassium fluoride dihydrate was supplied by Lachema and converted to anhydrous salt by heating under vacuum. Chlorosulfuric acid 98% was supplied by Fluka. Trifluoromethane sulfonamide was supplied by Rhodia and tetraphenylphosphonium chloride by Lachema.

^{19}F NMR spectra were recorded in THF using a Bruker AVANCE DRX 300 instrument.



2 3

Scheme 2. Synthesis of potassium N-(fluorosulfuryl)trifluoromethane sulfonamide (**3**).



3 4

Scheme 3. The synthesis of tetraphenylphosphonium N-(fluorosulfuryl)trifluoromethane sulfonamide (**4**) from (**3**).

Table 1
Crystal data and structure refinement for Ph_4P^+ $CF_3SO_2N^-SO_2F$ (**4**).

Empirical formula	$C_{25}H_{20}F_4NO_4PS_2$
Formula weight	569.51
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	tetragonal
Space group	$P\bar{4}$
Unit cell dimensions	
a (Å)	18.600(3)
b (Å)	18.600(3)
c (Å)	7.0782(14)
α (°)	90°
β (°)	90°
γ (°)	90°
Volume (Å^3)	2448.7(7)
Z	4
Calculated density (mg/m^3)	1.545
Absorption coefficient (mm^{-1})	0.348
F(0 0 0)	1168
Crystal size (mm)	0.1 × 0.07 × 0.05
θ Range for data collection	3.46–24.99°
Limiting indices	$-22 \leqslant h \leqslant 16$ $-22 \leqslant k \leqslant 22$ $-8 \leqslant l \leqslant 8$
Reflections collected/unique	13952/4316 [R_{int} = 0.1054]
Completeness to Θ = 25.00	99.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4316/0/334
Goodness-of-fit on F^2	0.752
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0548, wR_2 = 0.0604
R indices (all data)	R_1 = 0.1286, wR_2 = 0.0791
Absolute structure parameter	0.11(11)
Largest difference in peak and hole (e Å^{-3})	0.378 and −0.284

Raman spectra were recorded on a FT-IR Bruker EQUINOX IFS 55/S spectrometer with FRA 106/S equipment using Nd:YAG laser (k = 1064 nm), maximal output 500 mW. Samples were measured in glass ampoules. Intensity data were collected on a KUMA KM-4 j-axis diffractometer equipped with CCD detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 120 K. The structure was solved by direct methods and refined anisotropically by full-matrix least-squares method. The software packages used were: XCALIBUR CCD system for the data collection/reduction [7], and SHELXTL V5.1 system for the structure solution, refinement, and drawings (thermal ellipsoids are drawn at the 50% probability level) [8].

3.1. *N-(chlorosulfuryl)trifluoromethane sulfonamide* $CF_3SO_2NHSO_2Cl$ (**2**)

About 7.5 g (0.05 mol) trifluoromethane sulfonamide (**1**) was suspended in 6 ml (0.08 mol) thionyl dichloride and 3.3 ml (0.05 mol) chlorosulfuric acid was added. The mixture was heated in oil bath (140 °C) for 22 h under reflux condenser closed with $CaCl_2$ drying tube. Light brown reaction mixture was formed and $SOCl_2$ was removed by vacuum distillation (650 Pa, 70 °C). After cooling, the compound (**2**) crystallized from a viscous residue. Then, (**2**) was recrystallized from 15 ml of hot tetrachloromethane. White, crystalline product was washed with 5 ml CCl_4 and dried by 650 Pa. Yield 8.6 g (69%).

^{19}F NMR (CH_2Cl_2): −75.49 ppm (singlet); Raman: 135 (s), 261 (w), 268 (m), 297 (m), 323 (m), 358 (w), 381 (w), 420 (vs), 546 (vw), 558 (vw), 576 (w), 602 (vw), 629 (vw), 772 (vs), 819 (vw, br), 1116 (vw), 1180 (w), 1236 (s), 1314 (vw), 1422 (vw), 1441 (w).

3.2. *Potassium N-(fluorosulfuryl)trifluoromethane sulfonamide* $K[CF_3SO_2NSO_2F]$ (**3**)

About 15 g (0.26 mol) of finely powdered anhydrous potassium fluoride was suspended in 20 ml dichloromethane and crude (non-recrystallized) $CF_3SO_2NHSO_2Cl$ (**2**), prepared from 7.5 g (0.05 mol) trifluoromethane sulfonamide (**1**), and 20 ml dichloromethane, were added under vigorous stirring. Dichloromethane was subsequently distilled off at 650 Pa. Then, the solid residue was heated on oil bath (170 °C, 650 Pa) for 2 h. A 15 ml of dry *n*-butylacetate was added to the hot pasty grey mixture and the mixture was homogenized with a glass stick. After cooling, the mixture was three times extracted with 15 ml tetrahydrofurane portions. Combined extracts were evaporated in vacuum (2 kPa, 60 °C) until crystallization began. About 50 ml dichloromethane was added under constant stirring, the white solid was filtered off, washed with dichloromethane and dried in vacuum at 650 Pa. Yield 11.3 g (83.5%).

^{19}F NMR (THF): 55.6 ppm (quartet, J_{FF} = 5 Hz, Int. = 33.6), −79.6 ppm (doublet, J_{FF} = 5 Hz, Int. = 97.2); Raman: 178 (vw, br), 286 (m), 314 (w), 329 (m), 342 (m), 402 (w, br), 420 (vw), 478 (vw), 541 (vw), 556 (vw), 573 (vw), 616 (vw), 636 (vw), 743 (vs), 858 (vw), 1144 (vw), 1191 (w), 1237 (s), 1325 (vw), 1362 (vw).

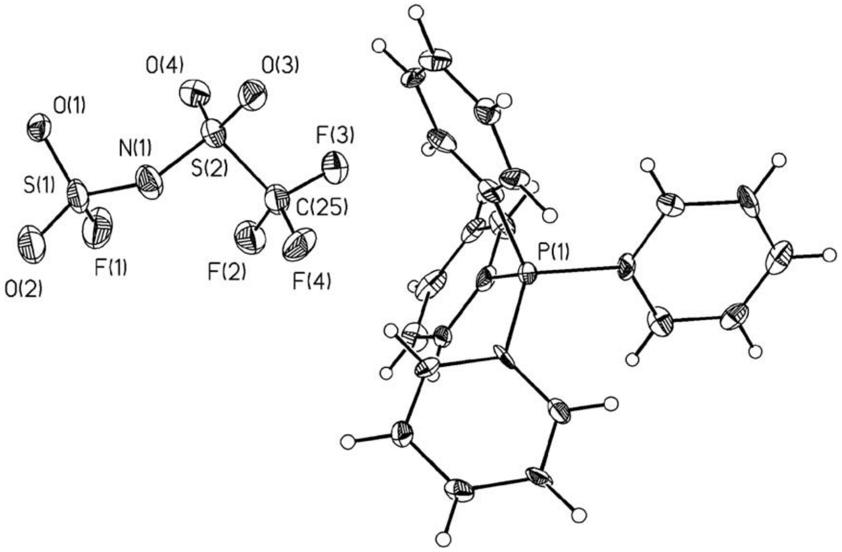


Fig. 1. The molecular structure of Ph_4P^+ $CF_3SO_2N^-SO_2F$ (**4**). Thermal ellipsoids are drawn on the 50% probability level.

Table 2
Bond lengths [Å] and angles [°] for (**4**) and bis(fluorosulfuryl) imides.

	$Ph_4P^+CF_3SO_2N^-SO_2F$ (**4**)	$HN(SO_2F)_2$ [9]	$LiN(SO_2F)_2$ [2]	$KN(SO_2F)_2$ [9]	$CsN(SO_2F)_2$ [10]
S1–O1	1.471(4)	1.404(3)	1.409(1)	1.413(7)	1.406(2)
S1–O2	1.394(5)	1.403(8)	1.423(1)	1.378(5)	1.419(2)
S–O bond length (second SO_2F group)		1.392(2)	1.410(1)	1.395(2)	1.416(2)
		1.413(2)	1.422(1)	1.413(8)	1.388(2)
S1–N1	1.540(5)	1.612(3)	1.556(2)	1.558(3)	1.558(2)
S–N bond length (second SO_2F group)		1.642(1)	1.556(2)	1.577(2)	1.576(2)
S1–F1	1.510(4)	1.511(1)	1.541(1)	1.557(3)	1.518(8)
S–F bond length (second SO_2F group)		1.516(4)	1.541(1)	1.569(3)	1.560(2)
S2–O3	1.416(4)	–	–	–	–
S2–O4	1.446(4)	–	–	–	–
S2–N1	1.572(6)	–	–	–	–
S2–C25	1.758(7)	–	–	–	–
C25–F2	1.361(7)	–	–	–	–
C25–F3	1.348(7)	–	–	–	–
C25–F4	1.337(7)	–	–	–	–
O1–S1–O2	112.1(3)	123.2(2)	118.1(1)	118.3(2)	119.7(2)
O–S–O angle (second SO_2F group)		123.9(2)	118.1(1)	120.1(2)	119.3(1)
O3–S2–O4	117.8(3)	–	–	–	–
S1–N1–S2	123.5(4)	123.4(2)	123.0(1)	124.2(2)	120.8(2)

*3.3. Tetraphenylphosphonium N-(fluorosulfuryl)trifluoromethane sulfonamide $Ph_4P[CF_3SO_2NSO_2F]$ (**4**)*

Solution of 2.4 g (6.4 mmol) of tetraphenylphosphonium chloride in 20 ml water was mixed with 10 ml dichloromethane and the solution of 1.7 g (6.3 mmol) of potassium N-(fluorosulfuryl)trifluoromethane sulfonamide (**3**) in 10 ml water was added under constant stirring. White precipitate was formed in the course of reaction and was quickly dissolved in dichloromethane that was present in the reaction mixture. The organic phase was subsequently separated and the aqueous phase was three times extracted with 10 ml dichloromethane portions. Combined organic extracts were dried by anhydrous $MgSO_4$ and the solvent was partially removed in vacuum (2 kPa, 40 °C) to obtain final volume of *ca* 5 ml. Then, 25 ml diethylether was slowly added under constant stirring. White, crystalline product was precipitated. It was filtered off, washed with ether (3 × 10 ml) and dried at 650 Pa. Yield 2.7 g (74%) of white needle-like crystals.

^{19}F NMR (THF): 55.97 ppm (singlet), −79.07 ppm (singlet); Raman: 111 (s, br), 199 (w, br), 249 (w), 260 (vw), 293 (vw), 324 (vw), 347 (vw), 615 (w), 679 (w), 711 (vw), 724 (vw), 757 (vw), 999 (vs), 1027 (m), 1097 (w), 1108 (vw), 1163 (vw), 1187 (vw, br), 1238 (vw, br), 1317 (vw), 1343 (vw), 1437 (vw), 1577 (w), 1586 (m).

Crystals for X-ray diffraction were grown by using diffusive method. Solution of tetraphenylphosphonium N-(fluorosulfuryl)trifluoromethane sulfonamide (**4**) in dichloromethane was carefully overlaid with great excess of ether. The vessel (test tube) was hermetically closed and allowed to stand at rest. After several weeks the crystals were separated and used for X-ray diffraction. However, the crystals were of poor quality as witnessed by R_{int} and R_σ values (Table 1). Thus, some structural parameters are not of a commonly accepted precision.

Supplementary material

CCDC 710001 contains the supplementary crystallographic data for tetraphenylphosphonium N-(fluorosulfuryl)trifluoromethane sulfonamide, $Ph_4P[CF_3SO_2NSO_2F]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

This work was supported by the Institutional Research Plan AV0Z40310501.

References

[1] M. Beran, J. Příhoda, Z. Anorg. Allg. Chem. 631 (2005) 55.
[2] M. Beran, J. Příhoda, Z. Žák, M. Černík, Polyhedron 25 (2006) 1292.
[3] H.W. Roesky, H.H. Giere, Inorg. Nucl. Chem. Lett. 7 (1971) 171.
[4] J. Taraba, Z. Žák, Acta Crystallogr., Sect. C 60 (2004) o79.
[5] A. Růžička, L. Zatloukalová, Z. Chem. 27 (1987) 227.
[6] R. Faggiani, D.K. Kennepohl, C.J.L. Lock, et al., Inorg. Chem. 25 (1986) 563.
[7] XCALIBUR CCD System, CRYSALIS Software System, Version 1.168, Oxford Diffraction Ltd., Oxford, England, 2001.
[8] SHELXTL, Version 5.10, Bruker AXS Inc., Madison, WI, USA, 1997.
[9] Z. Žák, A. Růžička, Ch. Michot, Z. Krist. 213 (1998) 217.
[10] O. Hiemisch, D. Henschel, A. Blaschette, P.G. Jones, Z. Anorg. Allg. Chem. 623 (1997) 324.