2.0 mmol) was added 2-thienyllithium (2 mL, 1.0 M in THF) at $-30\,^{\circ}C$, and the mixture was stirred for 30 min. The organozinc reagent was centrifuged for 2 min (2500 rpm), and the content of the tube was transferred by cannula to the flask containing Li(2-Th)CuCN at $-30\,^{\circ}C$. A solution of 2-cyclohexenone (202.4 mg, 2.0 mmol) and TMSCl (439 mg, 4.0 mmol) was then added to the flask. The reaction was allowed to warm slowly to room temperature for one day. An additional aliquot of the electrophilic mixture (0.5 equiv) was added, and the reaction was allowed to stir for two more days. The mixture was then hydrolyzed (2 M HCl) and extracted with diethyl ether (2×100 mL), the organic phases were dried ($MgSO_4$), and the solvents were removed (15 torr, $30\,^{\circ}C$). Impure **6** was isolated by column chromatography (Florisil, hexanes/ethyl acetate). By-products were removed by shaking a solution of the impure compound in hexane (50 mL) with a methanolic solution of mercurium(II) acetate (≈ 0.25 M, 25 mL) for 5 min. Addition of water (50 mL) and extraction with diethyl ether ($2 \times$ 100 mL) afforded, after drying ($MgSO_4$) and elimination of solvents, pure **6** (375 mg, 65 %).

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The Crystal Structures of Peroxonium Hexafluoroantimonate $H_3O_2SbF_6$ and Bis(dihydrogenperoxo)hydrogen Hexafluoroantimonate $H_5O_4SbF_6$

Rolf Minkwitz,* Claudia Hirsch, and Hans Hartl

The preparation of peroxonium salts by direct protonation of hydrogen peroxide was accomplished by Christe et al.[1] in 1979 [Eq. (a)]. These salts were characterized by IR, Raman and NMR spectroscopy. Two O – O stretching vibrations at 876 and 915 cm^{-1} were observed in the IR spectrum of peroxonium hexafluoroantimonate and one vibration at 879 cm^{-1} in the Raman spectrum, although the less intensive vibration at 915 cm^{-1} could not be assigned (Table 1). Therefore we decided to examine this salt more closely.

$$H_2O_2 + HF/MF_5 \xrightarrow{HF} H_3O_2^+MF_6^- \quad (a)$$
$$M = As, Sb$$

To avoid the danger of explosion that can arise from the use of highly concentrated hydrogen peroxide, and to ensure that there is no production of $H_3O^+SbF_6^-$ due to traces of water, we decided to use bis(trimethylsilyl)peroxide as the substrate [Eq. (b)]. The crystalline reaction product shows vibrations at 875 and 914 cm^{-1} in the IR spectrum and at 877 and 911 cm^{-1} in the Raman spectrum (Table 1).

$$Me_3SiOOSiMe_3 + 3\,HF + SbF_5 \xrightarrow{HF/-70\,^{\circ}C} \underset{\mathbf{1}}{H_3O_2^+SbF_6^-} + 2\,Me_3SiF \quad (b)$$

Careful examination of the product under a microscope in a stream of cold nitrogen indicated that there were, in addition to crystals[2] of the expected product **1,** some other crystals with a slightly different habit. The composition of these crystals was determined to be $H_5O_4^+SbF_6^-$ (**2**) by structure elucidation,[3] and subsequently **2** was prepared in the pure form by the reaction described in Equation (c), in which double the amount of bis(trimethylsilyl)peroxide was used relative to SbF_5 (cf. [Eq. (b)].

$$2\,Me_3SiOOSiMe_3 + 5\,HF + SbF_5 \xrightarrow{HF/-70\,^{\circ}C} \underset{\mathbf{2}}{H_5O_4^+SbF_6^-} + 4\,Me_3SiF \quad (c)$$

The Raman spectrum of **2** shows no vibration at 879 cm^{-1} but instead one at 908 cm^{-1}. In contrast, the vibration at 874 cm^{-1} in the IR spectrum is retained and no further vibrations were detected in this area (Table 1).

The $H_3O_2^+$ ion and the SbF_6^- ion in the crystal structure of **1** are donor and acceptor for two short hydrogen bonds (O1–H ··· F2 252.1(8) pm and O1–H ··· F4 252.3(8) pm), and for one longer hydrogen bond (O2–H ··· F3 270.8(8) pm). The

[*] Prof. R. Minkwitz, Dipl.-Chem. Claudia Hirsch
Institut für Anorganische Chemie der Universität
Otto-Hahn-Strasse 6, D-44221 Dortmund (Germany)
Fax: (+49) 231-755-3797
Prof. H. Hartl
Institut für Anorganische und Analytische Chemie
der Freie Universität Berlin (Germany)

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Table 1. Vibrational frequencies of the peroxonium salts **1** and **2** [cm^{-1}] at various temperatures.

1		**1**[1]		**2**		ν[a]
IR	Ra	IR	Ra	IR	Ra	
$T = 223$ K	$T = 195$ K	$T = 77$ K	$T = 163$ K	$T = 223$ K	$T = 195$ K	
3453 mw	3462 (2)	3440 sh		3454 m	3459 (4)	$\nu(OH_2)$
3391 m	3397 (2)	3400 – 3150		3393 m		$\nu(OH_2)$
		vs				
	3262 (1)	3230 vs				ν(OH)
				3201 m		ν(OH)
				3144 m		ν(OH)
				3049 m		ν(OH)
				2829 vw		
				2360 w		
1549 w						$\delta_S(OH_2)$[b]
1427 m		1421 mw		1422 s	1429 (1)	δ(OOH)
					1409 (1)	δ(OOH)
1267 vw		1280 w		1272 w		$\tau(OH_2)$
1155 m		1126 mw		1135 s		$\delta_B(OH_2)$[b]
		1065 sh				$\rho(OH_2)$
		965 sh				
914 vw	911 (2)	915 w			908 (4)	ν(OO)
875 m	877 (8)	876 mw	879 (8.6)	874 ms		ν(OO)
						$\gamma(OH_2)$
373 w		375 mw				τ(OOH)
	688 (3)		689 (5)			
679 vs	675 (10)		677 (10)		670 (3)	
	663 (5)	666 vs		668 vs	660 (10)	
646 sh	643 (5)		642 (7)	643 m	638 (1)	
		615 s				
	561 (1)	571 ms	560 (2)	574 m	561 (1)	
525 sh		514 m		519 w		
453 sh						
			326 (1)			anion
310 m	294 (2)	309 ms		303 m	290 (2)	
280 m	284 (3)		283 (5)	279 s		
	266 (1)		263 (0.9)			
215 m			226 (0.5)			
193 m	201 (1)		200 (1.5)		190 (1)	
	172 (2)		174 (3.2)		165 (1)	
	124 (1)		126 (2.4)			
					107 (1)	

[a] Proposed assignments. [b] δ_S and δ_B are deformation and bending vibrations. vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, mw = medium weak, sh = shoulder.

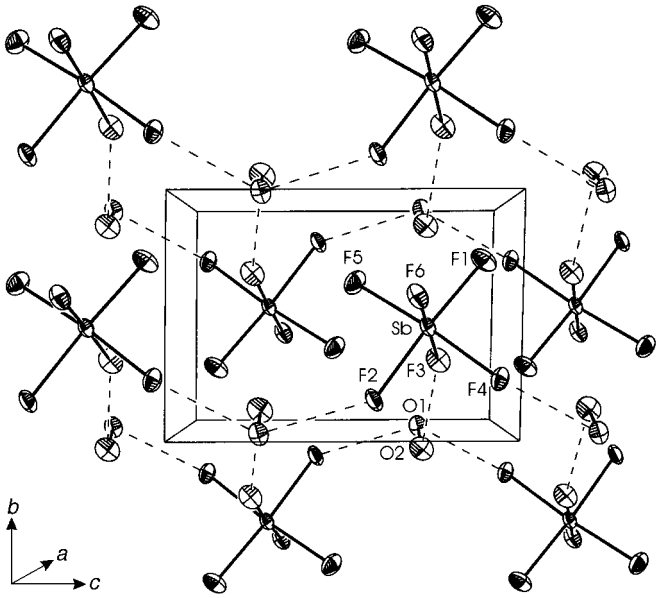

Figure 1. Section of the crystal structure of **1** (50% probability ellipsoids, H atoms are not shown). Distances [pm]: O1–O2 144.3(9), O1–F2 252.1(8), O2–F4 252.3(8), O2–F3 270.8(9).

hydrogen bonds link the cations and anions to form corrugated bands of centrosymmetric ten-membered rings that run parallel to the *ac* plane (Figure 1). Similar linkages exist in the low-temperature structure of oxonium hexafluoroarsenate[4] and in the structure of oxonium tetrafluoroborate.[5] None of the other interionic contacts is smaller than the sum of the van der Waals radii. As expected, the Sb–F bonds of the fluorine atoms that participate in short hydrogen bonds (191.3(5) and 191.2(5) pm) in the extremely distorted octahedral SbF_6^- ion are significantly longer than the other Sb–F bond lengths (185.5(5) – 187.3(5) pm). All three hydrogen atoms of the $H_3O_2^+$ ion are linked by hydrogen bonds to the SbF_6^- ion. The cation can be assumed to have an antiperiplanar conformation if the hydrogen atoms, only one of which was detected from the difference Fourier map, lie on the connecting line of the O–F contacts. The O–O bond length is 144.3(9) pm and is slightly shorter than the distance in free hydrogen peroxide, as determined by X-ray diffraction (146.1(3) pm) and neutron diffraction (145.8(4) pm).[6] This indicates that the weak O–O bond in hydrogen peroxide is strengthened by conversion of the lone pair of electrons into a bonding electron pair in **1**.

The triclinic centrosymmetric unit cell of **2** contains, in addition to two crystallographically equivalent SbF_6^- ions, two crystallographically independent bis(dihydrogenperoxo)hydrogen cations linked by weak hydrogen bonds (O1–H ··· O3 287.0(5) pm) to form chains with C_i symmetry. In this case, all the hydrogen atoms were located in a difference Fourier map.

The positional parameters and therefore the O–H bond lengths could only be determined with low accuracy and so, as in **1**, the O–O or O–F bond lengths were used to assess the strength of the hydrogen bond.

Split atomic positions were determined for the bridging hydrogen atoms (Figure 2). The two $H_5O_4^+$ ions are shaped

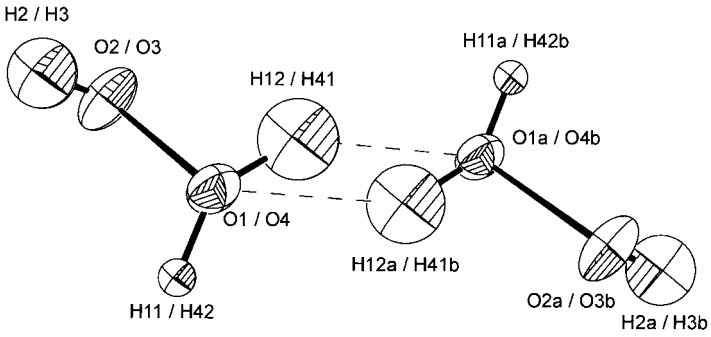

Figure 2. Structure of the $H_5O_4^+$ ion (50% probability ellipsoids for the oxygen atoms, 25% probability ellipsoids for the hydrogen atoms, the double atom designation is due to the two crystallographically independent $H_5O_4^+$ ions; the hydrogen atom positions H12/H41 and H12a/H41b are each half occupied). Distances [pm]: O1–O2 145.0(7), O3–O4 145.7(5); torsion angles [°]: H2-O2-O1-H12 138(15), H3-O3-O4-H41 90(15), H2-O2-O1-H11 – 80(13), H3-O3-O4-H42 – 109(8); atoms created by symmetry: a: $-x+1$, $-y$, $-z+1$, b: $-x$, $-y$, $-z$.

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like the analogous diaquahydrogen $H_5O_2^+$ ion, and form centrosymmetric units with one unsymmetrical disordered hydrogen bond per unit (O1–H···O1a 240.8(5) and O4–H···O4b 244.6(6) pm). Similar disorder was observed in the crystal structure of trifluoroacetic acid tetrahydrate.[7] The O–O bond lengths (145.0(7) and 145.7(5) pm) are slightly longer than in **1** but shorter than in hydrogen peroxide.[6]

The cation is both a donor and an acceptor of hydrogen bonds and cation-linked ten-membered rings are formed (Figure 3), which are three-dimensionally linked by weaker

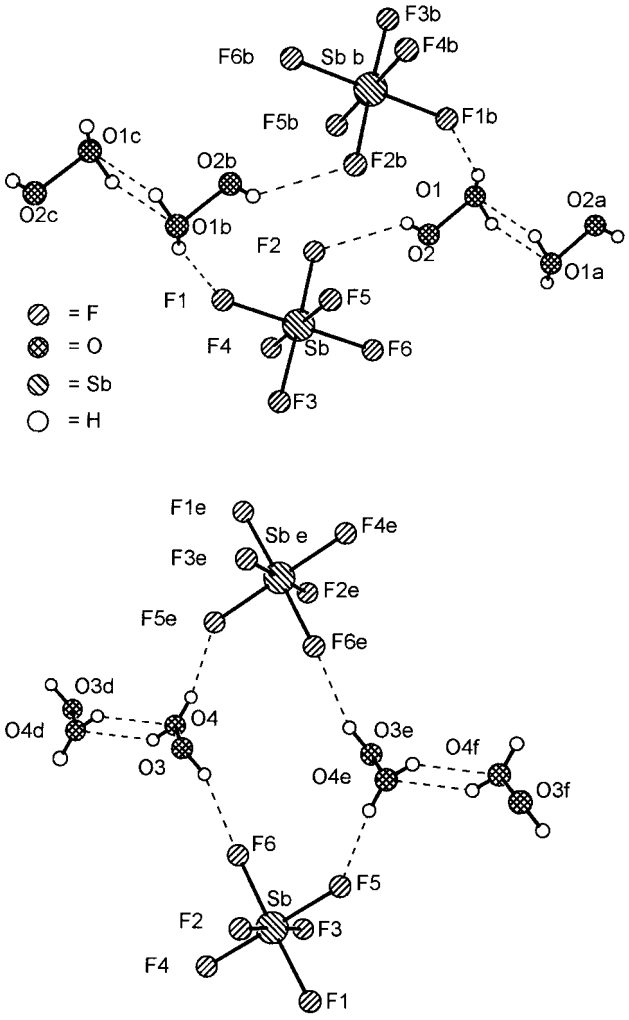

Figure 3. View of the two ten-membered rings in **2**. Distances [pm]: O1b–F1 266.7(6), O2–F2 270.7(6), O3–F6 278.5(5), O4e–F5 270.5(6); atoms created by symmetry: a: $-x+1, -y, -z+1$, b: $-x+1, -y+1, -z+2$, c: $x, y+1, z+1$, d: $-x, -y, -z$, e: $-x, -y, -z+1$, f: $x, y, z+1$.

O–H···O hydrogen bonds (Figure 4). In addition, the O–H···F hydrogen bonds with O–F distances of between 266.7(6) and 296.8(6) pm result in complex cross-linking between the cations and anions. The SbF_6^- ion is a slightly distorted octahedron. The Sb–F bond length (189.9(3) pm) of the F atom that is involved in the shortest hydrogen bond, is only slightly longer than the other Sb–F distances (186.4(3) pm – 188.0(3) pm).

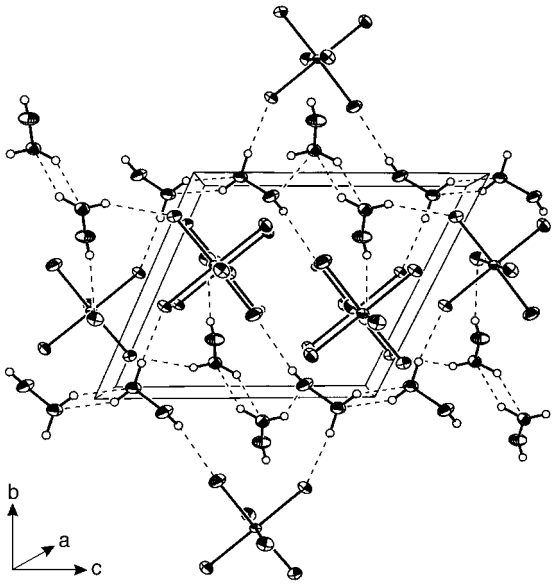

Figure 4. Section of the crystal structure of **2** (50 % probability ellipsoids for all atoms except hydrogen).

Experimental Section

Bis(trimethylsilyl)peroxide was prepared from hexamethylene tetramine, hydrogen peroxide, and trimethylchlorosilane.[8] SbF_5 was distilled several times, and HF was dried with F_2.

1: SbF_5 (1 mmol) was dissolved in HF (2 g) and placed in a 30- mL-KEL-F-reactor dried with F_2. After condensation of bis(trimethylsilyl)peroxide (1 mmol) at 77 K, the reaction mixture was warmed slowly to 203 K. The peroxonium salt was formed as a colorless solid. The trimethylfluorosilane and the excess HF were removed at 195 K under dynamic vacuum conditions.

The preparation of **2** was carried out in the same way as the preparation of **1** but with 2 mmol bis(trimethylsilyl)peroxide.

Equipment: Raman: Jobin-Yvon T64000, Ar^+ Laser ($\lambda = 514{,}5$ nm), Spectra Physics; IR: Bruker IFS 113v.

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[3] a) X-ray data of **2** at 125 K: $M_r = 304.79$, triclinic, space group $P\bar{1}$, $a = 658.0(2)$, $b = 781.3(85)$, $c = 821.6(3)$ pm, $\alpha = 110.51(4)$, $\beta = 95.04(3)$, $\gamma = 113.90(4)^\circ$, $V = 0.34842$ nm^3, $Z = 2$, $\rho_{calcd} = 2.905$ Mg m^{-3}, crystal dimensions $0.67 \times 0.3 \times 0.1$ mm^3, $\mu(Mo_{K\alpha}) = 4.054$ mm^{-1}, $F(000) = 284$, 2246 measured reflections, 2107 independent reflections, and 2046 with $F_o > 4\sigma(F_o)$, $R_1 = 0.0397$ (all data: 0.0415), $wR_2 = 0.1222$, $S = 0.892$. b) Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-40854 (**1**) and CSD-40854 (**2**).

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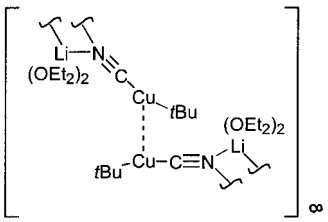
The Crystal Structures of a Lower Order and a "Higher Order" Cyanocuprate: $[t\text{BuCu(CN)Li(OEt}_2)_2]_\infty$ and $[t\text{BuCu}t\text{Bu\{Li(thf)(pmdeta)\}}_2\text{CN}]$**

Gernot Boche,* Ferdinand Bosold, Michael Marsch, and Klaus Harms

Cyanocuprates are an important class of cuprates because of their significance in organic synthesis.[1] On the basis of their different composition and reactivity they can be divided into two groups:[2] lower order cyanocuprates of the type RCu(CN)Li, with RLi and CuCN units in a 1:1 ratio, and "higher order" cyanocuprates of the type $R_2Cu(CN)Li_2$, with RLi and CuCN units in a 2:1 ratio. In recent years the structure of the latter has been the topic of much investigation and controversial discussion:[3] Do these compounds have a special reactivity due to a bis-anion character? EXAFS,[4] NMR,[5] and IR spectroscopic investigations[6] indicated that the major proportion of the Cu atoms (>90%) is not bonded to the cyanide ion, and thus $R_2Cu(CN)Li_2$ more likely exists as "RCuR-Li+LiCN" rather than with a three-coordinate Cu atom. This is consistent with quantum-chemical calculations which show **1** to be the most stable structure.[4c, 7] Recent cryoscopic investigations in tetrahydrofuran at −108 °C demonstrated that lower order cyanocuprates exist as a monomer [*t*BuCu(CN)Li] or as a dimer [(PhCu(CN)Li)$_2$]. For the higher order cyanocuprates $R_2Cu(CN)Li_2$, cryoscopy revealed monomeric species (R = Me,Ph); however, in the case of R = *t*Bu there is the possibility of a fast equilibrium between a higher order and a lower order cyanocuprate.[8] While only a few solid-state structures of Gilman cuprates containing the free structural element R_2Cu^- exist,[9] no crystal structures of cyanocuprates have been described yet. Here we report on the crystal structures of [*t*Bu-Cu(CN)Li · $(OEt_2)_2]_\infty$ (**2**), a lower order cyanocuprate, and [*t*BuCu*t*Bu{Li(thf)(pmdeta)$_2$CN}] (**3**, pmdeta = pentamethyldiethylenetriamine), a compound of the type $R_2Cu(CN)Li_2$.



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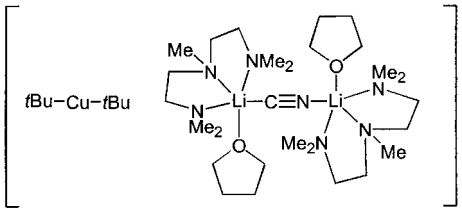

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Figure 1 shows a section of the crystal structure of **2.**[10a] The *t*Bu group (Cu1 – C2 196.9(7) pm) and the cyanide ion (Cu1 – C1 187.8(8) pm) are bonded to the Cu atom. The N1 atom of the cyanide group (C1 – N1 115.9(9) pm) is coordinated to two Li cations (Li1 and Li1A), each of which is complexed by two diethyl ether molecules. By the formation of the four-membered ring N1-Li1-N1A-Li1A, an additional molecule is bound. The mutual arrangement of the two cyanocuprate units C2-Cu1-C1-N1 and C7-Cu2-C6-N2 is of particular interest. In both cuprates the angles C1-Cu1-C2 and C6-Cu2-C7 (170.0(3) and 168.0(3)°, respectively) are less than 180°, while the dihedral angles C1-Cu1-Cu2-C6 and C1-Cu1-Cu2-C7 are 84.8(3) and −94.9(3)°, indicating an almost perpendicular relative arrangement of the two cyanocuprates. The angle C1-Cu1-Cu2 (C6-Cu2-Cu1) amounts to 86.5(2)° (88.4(2)°), while that involving the *t*Bu groups (C7-Cu2-Cu1

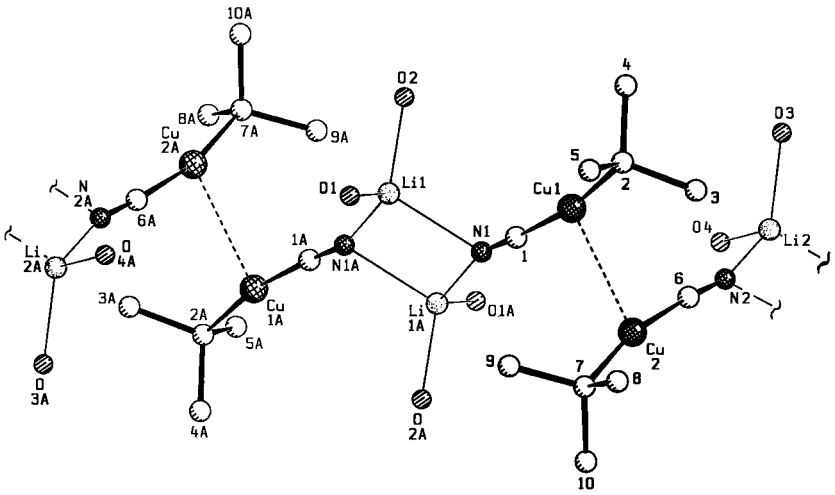

Figure 1. Section of the crystal structure of **2**. The ethyl groups of the diethyl ether molecules have been omitted for clarity.

[*] Prof. Dr. G. Boche, F. Bosold, M. Marsch, Dr. K. Harms
Fachbereich Chemie der Universität
D-35032 Marburg
Fax: (+49) 6421-288917
E-mail: boche@ps1515.chemie.uni-marburg.de

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