Angewandte Chemie

DOI: 10.1002/anie.200906863

Silver(II) Compounds

$Ag^{II}SO_4$: A Genuine Sulfate of Divalent Silver with Anomalously Strong One-Dimensional Antiferromagnetic Interactions[**]

*Przemysław J. Malinowski, Mariana Derzsi, Zoran Mazej, Zvonko Jagličić, Bartłomiej Gaweł, Wiesław Łasocha, and Wojciech Grochala**

In memory of Jan Czochralski

The chemistry of coinage metals is rich and surprising, and considerable differences are found between copper, silver, and gold.[1] Among the compounds of Group 11 metals, those of divalent silver are in many ways unique and owe their properties to the remarkable electron-withdrawing power of oxidizing silver(II).[2–4] As a consequence, many simple binary and ternary connections of divalent silver have not yet been prepared. Particularly intriguing is that a sulfate of silver(II) has not yet been synthesized, given that anhydrous $CuSO_4$ has been meticulously characterized in the past,[5] and the related $AuSO_4$ has been known for a decade.[6] This inconsistency is further emphasized by the fact that few other oxo derivatives of silver (II) are known, including fluorosulfate, triflate,[7] and oxoargentate(III), $Ag[AgO_2]_2$.[8] Indeed, it has been recently shown that inorganic sulfates resist the presence of Ag^{II} from AgF_2 up to fairly high temperatures of about 300 °C.[9] Herein we present two distinct synthetic pathways to $AgSO_4$, which is a genuine sulfate of divalent silver and neither a mixed-valence Ag^I/Ag^{III} compound nor the peroxodisulfate of Ag^I.[10]

Black $AgSO_4$ can be prepared by metathesis in anhydrous HF solvent:

$$Ag(SbF_6)_{2\,(aHF)} + K_2SO_{4\,(aHF)} \rightarrow AgSO_4\downarrow + 2\,KSbF_6 \qquad (1a)$$

or by displacement of a weaker acid by a stronger one:

$$AgF_2 + H_2SO_4 \rightarrow AgSO_4\downarrow + 2\,HF\uparrow \qquad (1b)$$

The product of Reaction (1 a) is contaminated by substantial amounts of amorphous $KSbF_6$ (see the Supporting Information); therefore, all results reported herein are for the superior-quality product of obtained from Reaction (1 b).

Table 1: Crystallographic data for $AgSO_4$.

$P\bar{1}$	$Z=2$	$V=151.761(6)$ Å^3		
a, b, c [Å]:	4.6923(1)	4.7535(1)	8.0125(2)	
α, β, γ [°]	103.403(1)	76.478(1)	118.078(1)	
Ag1 1a	0	0	0	
Ag2 1h	0.5	0.5	0.5	
S1 2i	0.1593(9)	−0.3276(11)	0.2508(6)	
O1 2i	−0.0787(17)	−0.6544(16)	0.1980(12)	
O2 2i	0.4286(19)	−0.337(2)	0.2989(9)	
O3 2i	0.2749(19)	−0.142(3)	0.1072(11)	
O4 2i	0.0017(13)	−0.1713(14)	0.4029(11)	
$R_p=6.12\%$	$R_{wp}=6.26\%$			
Ag1−O (Å):	2.107(8)	2.107(8)	2.113(13)	2.113(13)
Ag2−O (Å):	2.094(10)	2.094(10)	2.198(5)	2.198(5)
S−O (Å):	1.427(12)	1.457(7)	1.458(13)	1.503(8)

$AgSO_4$ crystallizes in the triclinic $P\bar{1}$ space group (Table 1 and Figure 1; for Rietveld refinement see the Supporting Information). The unit cell of silver(II) sulfate is the second smallest amongst the transition metal sulfates after $CdSO_4$. The closest Ag···Ag separation is as large as 4.6835(2) Å, thus preventing formation of the short metal–oxygen–metal bridges seen in homologous $CuSO_4$. The structure of $AgSO_4$ is also remarkably different from that of $AuSO_4$, which contains short Au−Au bonds. All oxygen atoms of the sulfate anion in $AgSO_4$ are utilized for bonding, in a similar fashion to $CdSO_4$ or $PdSO_4$, serving as O−S−O linkers between silver(II) cations, forming a three-dimensional network.[10] There are two non-equivalent silver atoms in the structure that are surrounded by oxide anions in a square-planar fashion, with Ag−O separations falling in a narrow range between 2.094(10) Å and 2.198(5) Å. Similarities in the coordination spheres of both silver centers suggests the $Ag^{II}SO_4$ formulation in contrast to the binary oxide "AgO", which is in fact the mixed-valence species $Ag^IAg^{III}O_2$.[11] The increased Lewis acidity of $AgSO_4$ ($AgO{\cdot}SO_3$) appears to prevent disproportionation[12] in a similar fashion to some gold(II) derivatives.[13]

The sulfate anion has four distinct S−O bonds that vary between 1.427(12) Å and 1.503(8) Å. This feature, superimposed on mutual interactions between similar frequency

---

[*] M. Derzsi, W. Grochala
ICM, The University of Warsaw (Poland)
Fax: (+48) 22-554-0801
E-mail: wg22@cornell.edu
P. J. Malinowski, W. Grochala
Faculty of Chemistry, the University of Warsaw (Poland)
Z. Mazej
Department of Inorganic Chemistry and Technology
Jožef Stefan Institute, Ljubljana (Slovenia)
Z. Jagličić
Institute of Mathematics, Physics and Mechanics
Jadranska 19, Ljubljana
and
University of Ljubljana, Faculty of Civil and Geodetic Engineering
Jamova 2, Ljubljana (Slovenia)
B. Gaweł, W. Łasocha
Faculty of Chemistry, Jagiellonian University, Cracow (Poland)

[**] The authors wish to acknowledge the TEAM program from FNP for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906863.

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

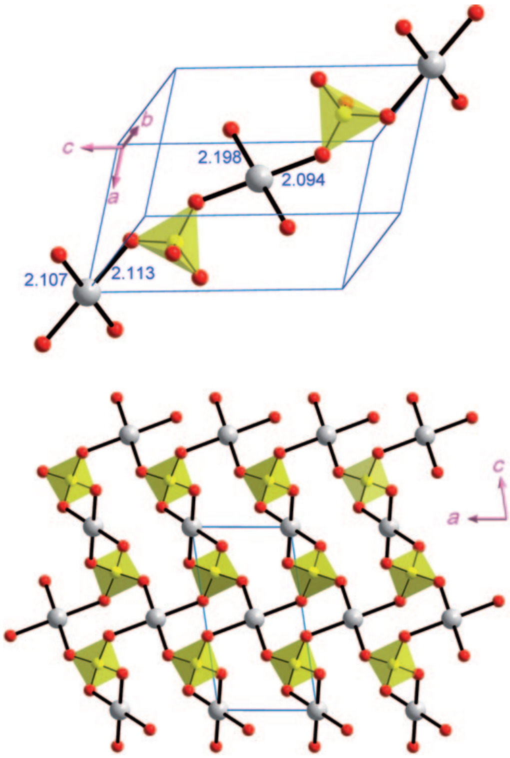

Figure 1. Top: Unit cell of $AgSO_4$, emphasizing propagation of one-dimensional $[Ag(SO_4)]_\infty$ chains along the main cell diagonal and the coordination spheres of Ag1 and Ag2. Bottom: Projection of the crystal structure of $AgSO_4$ on the *ac* plane, emphasizing connectivity of the network and absence of terminal oxygen atoms. Ag gray, O red, S yellow.

oscillators inside the unit cell (Z = 2), leads to splitting of the broad sulfate band (950–1200 cm^{-1}, S–O stretching vibrations) and of the bands corresponding to the O-S-O bending vibrations (500–700 cm^{-1}) in the MIR spectrum (Figure 2; for wavenumbers of the bands in the IR and Raman spectra of $AgSO_4$, see the Supporting Information).

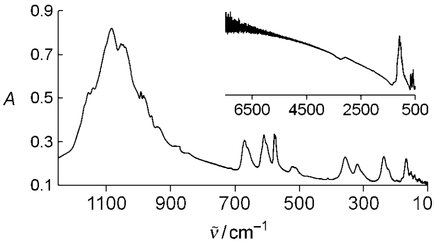

Figure 2. Far/mid IR and (inset) near IR spectra of $AgSO_4$.

A characteristic increase of absorbance above 1420 cm^{-1} (broad feature leveling off at about 7500 cm^{-1}; see Figure 2, inset) corresponds to a low-energy electronic excitation across the band gap of circa 0.18 eV. The charge-transfer nature of this excitation ($O^{2-} \rightarrow Ag^{2+}$; Ag^{II} is a potent oxidizer) is discussed below and in the Supporting Information. The low-energy electronic absorption explains deep black color of the compound,[14] but it also heralds its thermodynamic instability. Indeed, as deduced from thermogravimetric and differential scanning calorimetry (DSC) profiles (Figure 3 and Supporting Information), and from simultaneous evolved-gas analysis (consisting of IR and MS; Supporting Information), $AgSO_4$ decomposes exothermally above 120 °C ($Q = -26.5$ kJ mol^{-1}) with evolution of molecular oxygen. This observation suggests that $AgSO_4$ is thermodynamically unstable at ambient conditions owing to both enthalpy and entropy contributions to the Gibbs free energy.[10,15]

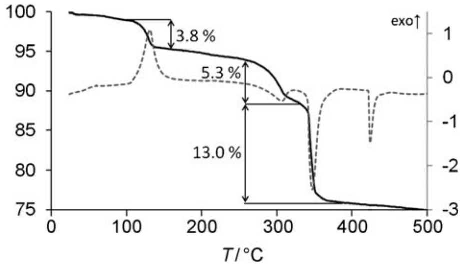

Figure 3. Thermal gravimetry curve (left scale; ——) and differential scanning calometry curve (right scale; -----) for $AgSO_4$. Heating rate: 10 K min^{-1}.

The mass loss during thermal decomposition of $AgSO_4$ is 3.8 wt %, which corresponds to the theoretical value of 3.9 wt % associated with the chemical reaction:

$$AgSO_4 \rightarrow 1/2\,Ag_2S_2O_7 + 1/2\,O_2\uparrow \qquad (2)$$

The crystalline decomposition product was confirmed to be the previously ill-characterized compound silver(I) pyrosulfate, $Ag_2S_2O_7$, by XRD and IR spectroscopy (Supporting Information). Upon further heating, this compound decomposes endothermally in two steps in the 250–370 °C temperature range with loss of 18.3 wt % (theoretical: 19.6 wt %[16]) in the form of SO_3:

$$Ag_2S_2O_7 \rightarrow Ag_2SO_4 + 1/2\,SO_3\uparrow \qquad (3)$$

The paramagnetic nature of divalent silver (electronic configuration $4d^9$) in $Ag^{II}SO_4$ raises questions about the strength of spin interactions. The temperature dependence of the magnetic susceptibility (Figure 4) shows that the magnetic behavior of $AgSO_4$ above 40 K can be fit well with a Bonner–Fisher model[17] of strongly antiferromagnetically coupled one-dimensional chains with isotropic interactions between nearest neighbors ($H = -2J\Sigma S_i S_j$). The obtained exchange integral is $J = -217$ K per pair of interacting Ag^{2+} cations (i.e., 9.5 meV per formula unit), whilst a value $g = 2.087$ was obtained from the ESR data.[18] The antiferromagnetic coupling, which is similar to that observed for various derivatives of Cu^{2+} or V^{4+},[19] persists even at temperatures around 100 °C at the onset of thermal decomposition. This observation is consistent with ESR spectra of $AgSO_4$ (Figure 4, inset), which show presence of a very broad (1.0–2.6 kG) antiferromagnetic signal centered around 3250 G

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

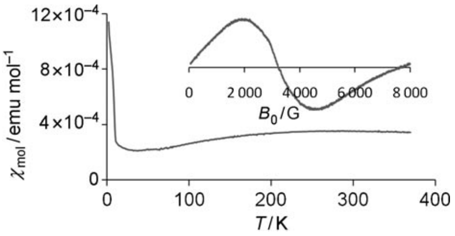

Figure 4. Temperature dependence of the magnetic susceptibility χ_{mol} and (inset) ESR spectrum of $AgSO_4$ at 292 K. The increase of susceptibility below 15 K is caused by an unknown magnetic impurity or by a phase transition.

($g = 2.087$) in the entire 2.4–292 K temperature range.[20] (For the temperature dependence of parameters of the ESR signal, see the Supporting Information).

The exchange integral $|J|$ between the nearest neighbors for $AgSO_4$ is over one order of magnitude higher than those previously observed for other transition metal sulfates. For example, sulfates of nickel(II), iron(II), and cobalt(II) order antiferromagnetically at 37 K, 21 K, and 15.5 K, respectively.[21] As each of these compounds contains between two or four unpaired electrons per transition metal cation (compared to one for $AgSO_4$), superexchange for $AgSO_4$ must thus be viewed as unusually strong. Even more striking is the contrast between $AgSO_4$ and $CuSO_4$: Anhydrous $CuSO_4$ orders antiferromagnetically below 36 K[5] despite the fact that magnetic superexchange in this compound takes place over direct oxo bridges, and not much longer covalent O–S–O linkers as in $AgSO_4$.

To gain insight into the nature of magnetic interactions and electronic band structure of $AgSO_4$, we performed spin-polarized DFT calculations using the GGA and GGA + U methods. Pathways for magnetic interactions are very complex; we therefore describe only the simplest model (Figure 5) with a magnetic unit cell identical to crystal unit cell. The artificially enforced antiferromagnetic state converged to a metallic solution within the GGA framework, as is typical for transition metal open-shell systems. However, the GGA + U calculations confirm an antiferromagnetic ground state of $AgSO_4$, with ferromagnetic and metallic solutions lying higher in energy by 3.1 meV and 20.3 meV per formula unit, respectively. The derived magnetic superexchange constant is 6.2 meV per one silver atom in the one-dimensional coupling model, and it is thus 1.5-fold underestimated relative to the experimental value. This discrepancy could certainly be decreased by allowing variation of semiempirical Mott–Hubbard U parameters for Ag(d), O(p), and S(p) electrons. The superexchange pathway involves the O–S–O bridge, but is largely over a direct O···O polarization, thus omitting the sulfur atom (Figure 5).

The calculated magnetic moments on the silver atoms ($-0.39\,\mu_B$ and $+0.44\,\mu_B$) are much smaller than those calculated for the copper atoms in $CuSO_4$ ($\pm 0.80\,\mu_B$), because spin density is considerably smeared over oxygen atoms for the former compound, but much less for the latter (see the Supporting Information).[22] Indeed, strongly oxidizing silver(II) easily introduces holes to oxygen-based bands, resulting in the lack of thermodynamic stability of $AgSO_4$ and evolution of O_2 upon its heating.

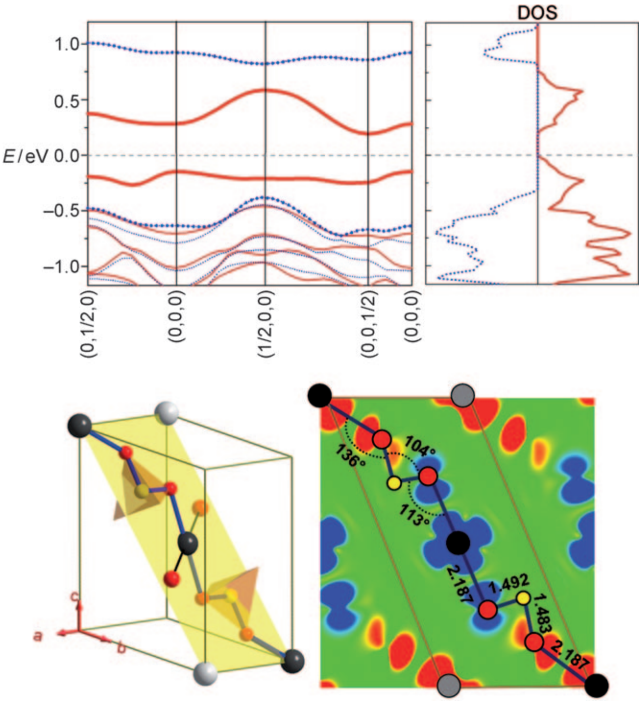

Figure 5. Top: The electronic band structure of $AgSO_4$. α red, β blue. Bottom: Projection of spin density on the 011 plane as calculated using spin-polarized GGA + U method. Red and blue colors correspond to the largest excess of α and β density, respectively.

The band structure of $AgSO_4$ shows that the uppermost two spin-majority and two spin-minority states are considerably separate from each other in the vicinity of the Fermi level. This result can be traced to the presence of two nonequivalent silver cations in the magnetic unit cell (Supporting Information). In consequence, the band gap between occupied (O-predominated) and unoccupied (Ag-predominated) α bands is much smaller than the corresponding gap for β states. The calculated band gap at the Fermi level of 0.18 eV agrees strikingly well with the experimental estimate, rendering $AgSO_4$ a narrow-band-gap magnetic semiconductor; it also explains the spin-allowed optical charge-transfer $\alpha \rightarrow \alpha$ absorption responsible for its black color. The band gap of $AgSO_4$ is one order of magnitude smaller than that of 2.34 eV calculated for $CuSO_4$ with the LSDA + U method (Supporting Information). Attempts are now ongoing in our laboratory to form a pressure-induced or chemical-doping-induced metallization of the $AgSO_4$ antiferromagnet.

Experimental Section

H_2SO_4 (95–98 %), AgF_2 (98 %), $K_2S_2O_7$ (99 %), and K_2SO_4 (99 %) were purchased from Sigma–Aldrich. $Ag(SbF_6)_2$ was synthesized from AgF_2[9] and SbF_5 in anhydrous HF (aHF).[23] HF was dried with K_2NiF_6 and distilled before use. Equipment used in the work is described elsewhere.[24]

$AgSO_4$ [Eq. (1 a)]: A mixture of $Ag(SbF_6)_2$, K_2SO_4, and solid HF at −196 °C was allowed to heat up inside a fluoropolymer reactor; a black precipitate formed immediately after the first droplets of liquid

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

HF formed at −83 °C. $AgSO_4$ was separated from crystalline $KSbF_6$ by-product by washing the latter away 18 times with aHF and dried.

$AgSO_4$ [Eq. (1b)]: The reaction between AgF_2 and H_2SO_4 was carried out inside an argon-filled glovebox. Fine AgF_2 powder was added slowly to a 13-fold excess of cold acid (−35 °C) to prevent a violent reaction. After the mixture stopped bubbling, the black precipitate was purified by washing away the remaining H_2SO_4 with aHF and drying.

DFT calculations: GGA and GGA + U calculations (VASP) were carried out for magnetic cell identical to the unit cell, with fractional atomic coordinates preoptimized at the GGA/PAW level (Supporting Information), and utilizing relativistic Vanderbildt-type pseudopotentials. Numerical parameters applied: cutoff 800 eV, k-point grid $4\times4\times2$, electronic convergence 10^{-7} eVatom^{-1}, $U(\mathrm{Ag}_{4d}) = U(\mathrm{O}_{2p}) = 4$ eV, $U(\mathrm{S}_{3p}) = 2$ eV, J(all atoms) = 1 eV.

Further details of the crystal structure may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the appropriate CSD number CSD-421341.

Received: December 5, 2009
Published online: January 18, 2010

Keywords: oxidation · silver · solid-state structures · superconductors

---

[1] P. Pyykkö, *Angew. Chem.* **2004**, *116*, 4512–4557; *Angew. Chem. Int. Ed.* **2004**, *43*, 4412–4456.

[2] B. Žemva, N. Bartlett, *Actual. Chim.* **2006**, *301*, 37–39.

[3] B. Müller, *Angew. Chem.* **1987**, *99*, 1120–1135; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1081–1097.

[4] W. Grochala, R. Hoffmann, *Angew. Chem.* **2001**, *113*, 2816–2859; *Angew. Chem. Int. Ed.* **2001**, *40*, 2742–2781.

[5] See for example an early account: F. Menzinger, D. E. Cox, B. C. Frazer, H. Umebayashi, *Phys. Rev.* **1969**, *181*, 936–945.

[6] M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2112–2114.

[7] P. C. Leung, F. Aubke, *Inorg. Chem.* **1978**, *17*, 1765–1772; P. C. Leung, F. Aubke, *Can. J. Chem.* **1979**, *57*, 326–335.

[8] B. Standke, M. Jansen, *Angew. Chem.* **1986**, *98*, 78–79; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 77–78; B. Standke, M. Jansen, *J. Solid State Chem.* **1987**, *67*, 278–284; G. I. N. Waterhouse, J. B. Metson, G. A. Bowmaker, *Polyhedron* **2007**, *26*, 3310–3322.

[9] P. Malinowski, Z. Mazej, W. Grochala, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2608–2616.

[10] Other theoretical results: M. Derzsi, K. Dymkowski, W. Grochala, unpublished results.

[11] K. Yvon, A. Bezinge, P. Tissot, P. Fischer, *J. Solid State Chem.* **1986**, *65*, 225–230.

[12] $AgSO_4$ cannot be obtained in the reaction using "AgO" and SO_3 substrates, even at −30 °C, as immediate evolution of O_2 and reduction of Ag^{II} is observed when these two solids come in contact with each other.

[13] AuF_2 is not stable to disproportionation, but its "acidified" $Au(SbF_6)_2$ form is: S. H. Elder, G. M. Lucier, F. J. Hollander, N. Bartlett, *J. Am. Chem. Soc.* **1997**, *119*, 1020–1026. See also: K. A. Barakat, T. R. Cundari, H. Rabaa, M. A. Omary, *J. Phys. Chem. B* **2006**, *110*, 14645–14651.

[14] Formation of black oxidizing solutions during electrolysis of Ag_2SO_4 dissolved in H_2SO_4 has been observed in the past, but $AgSO_4$ was not separated and identified.

[15] The first step of thermal decomposition of $Ag^{II}SO_4$ falls in a very similar temperature range to those of alkali metal peroxodisulfates, despite their very different chemical nature. The last DSC peak corresponds to a phase transition of Ag_2SO_4.

[16] Theoretical value related to initial mass of $AgSO_4$ and not of $Ag_2S_2O_7$.

[17] J. C. Bonner, M. E. Fisher, *Phys. Rev. A* **1964**, *135*, A640–A658.

[18] $AgSO_4$ starts decomposing very slowly above 50 °C, thus leading to a larger diamagnetic response above this temperature; in consequence, the true $|J|$ value is in fact slightly larger than the one derived herein. The characteristic magnetic response from traces of $^3O_2$ may be seen in magnetic susceptibility measurements for samples heated to almost 100 °C.

[19] I. Djerdj, M. Cao, X. Rocquefelte, R. Černý, Z. Jagličić, D. Arčon, A. Potočnik, F. Gozzo, M. Niederberger, *Chem. Mater.* **2009**, *21*, 3356–3369;J. Tong, C. Lee, M. H. Whangbo, R. K. Kremer, A. Simon, J. Köhler, *Solid State Sci.* **2010**, DOI: 10.1016/j.solidstatesciences.2009.02.028.

[20] J. S. Wells, L. M. Matarrese, D. J. Sukle, *J. Chem. Phys.* **1967**, *47*, 2259–2262.

[21] B. C. Frazer, P. J. Brown, *Phys. Rev.* **1962**, *125*, 1283–1291.

[22] $AgSO_4$ itself is a powerful oxidizer, as is apparent from several test reactions involving organic compounds. Remarkably, $AgSO_4$ can not be prepared by oxidizing Ag_2SO_4 in H_2SO_4 with $Ce^{IV}(SO_4)_2$.

[23] Z. Mazej, *J. Fluorine Chem.* **2004**, *125*, 1723–1733.

[24] Z. Mazej, E. Goreshnik, Z. Jagličić, B. Gaweł, W. Łasocha, D. Grzybowska, T. Jaroń, D. Kurzydłowski, P. J. Malinowski, W. Koźminski, J. Szydłowska, P. Leszczyński, W. Grochala, *CrystEngComm* **2009**, *11*, 1702–1710.

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim