Lewis Acids

Amorphous Aluminum Bromide Fluoride (ABF)**

*Thoralf Krahl and Erhard Kemnitz**

Dedicated to Professor Gerd-Volker Röschenthaler
on the occasion of his 60th birthday

Amorphous aluminum chloride fluoride (ACF; $AlCl_xF_{3-x}$, $x = 0.05–0.3$), which is of high interest for catalytic reactions,[1] was discovered at DuPont in 1992.[2] It exhibits an extraordinarily high Lewis acidity similar to the acidity of SbF_5, and in some cases, has even higher acidity. ACF is prepared by mild fluorination of $AlCl_3$ with chlorofluorocarbons such as $CFCl_3$. However, the fluorination is never carried out to completion; the solid phase always contains some chlorine. The high Lewis acidity is surprising since pure aluminum chloride and phases of aluminum fluorides prepared in other ways are much weaker Lewis acids. We recently reported the investigation of ACF by several spectroscopic methods[3] and presented our initial findings on the structure of this amorphous compound. However, the role of the residual chlorine in ACF is still unclear, but it has been shown that the structures of ACF and $AlCl_3$ differ with respect to the chlorine atoms.

Herein we report on the synthesis of amorphous aluminum bromide fluoride ABF ($AlBr_xF_{3-x}$, with $x = 0.13$), which is very similar to ACF. EXAFS measurements on the Br K edge of ABF enabled a more detailed study of the structure than for ACF. Partially fluorinated samples of $AlBr_3$ with the nominal composition $AlBr_2F$ and $AlBrF_2$ were also investigated. From the analysis of the data measured by ^{19}F MAS NMR spectroscopy and Br K EXAFS, together with that gained during the investigation of ACF,[3] a basic structural model of the compounds ABF and ACF is introduced for the first time.

Solid $AlBr_3$ is built up of discrete Al_2Br_6 molecules,[4a] whereas $AlCl_3$ has a layered structure.[4b] The fluorination of $AlBr_3$ with $CFCl_3$ is highly exothermic and can be performed similar to that of ACF [Eq. (1)] to initially give $CBrCl_3$ and ABF.

$$AlBr_3 + (3-x)\,CFCl_3 \rightarrow AlBr_xF_{3-x} + (3-x)\,CBrCl_3 \qquad (1)$$

The primary reaction product $CBrCl_3$ is not stable in the presence of a very strong Lewis acid such as ABF (see Experimental Section). Thus, it undergoes dismutation and slowly forms CCl_4, CBr_2Cl_2, CBr_3Cl, and CBr_4. These products have been observed by ^{13}C NMR spectroscopy. ABF is amorphous and shows no reflections in the XRD pattern. During heating, it crystallizes suddenly at 400 °C, forms crystalline β-AlF_3 and $AlBr_3$, and looses its very high Lewis acidity.

The Lewis acidity of ABF is very high. It catalyzes the isomerization reaction of 1,2-dibromohexafluoropropane to 2,2-dibromohexafluoropropane at room temperature [Eq. (2)], which requires an extremely strong Lewis acid.[1d]

$$CF_3-CFBr-CF_2Br \rightarrow CF_3-CBr_2-CF_3 \qquad (2)$$

We chose this particular reaction because it can be carried out relatively easily. The acidity of certain Lewis acids has been recently expressed quantitatively by calculation of the fluoride ion affinity (FIA) at the MP2 level of theory. From this point of view, molecular SbF_5 is the strongest Lewis acid with the highest FIA.[5] *Molecular* aluminum chloride and *molecular* aluminum fluoride have just slightly lower acidities. However, the acid strength of *solid* acids such as AlF_3, ACF, and ABF cannot be expressed in such terms, but a ranking of the acid strengths can be done in terms of their reactivity. Reaction (2) requires a highly acidic catalyst; it runs easily at room temperature with the very strong Lewis acids SbF_5, ACF, and ABF but not with the strong acids $AlCl_3$ and $AlBr_3$.

The IR spectrum of ABF (Figure 1) is typical for a network of corner-sharing AlF_6 octahedra,[3] which has the nominal composition of AlF_3. Two intensive bands at around 665 and 350 cm^{-1} are attributed to the valence and deformation vibrations of the AlF_6 octahedron, respectively. The large width of the band indicates the high degree of amorphicity of ABF. Interestingly, there is no significant difference between the IR spectra of ABF and ACF.[3]

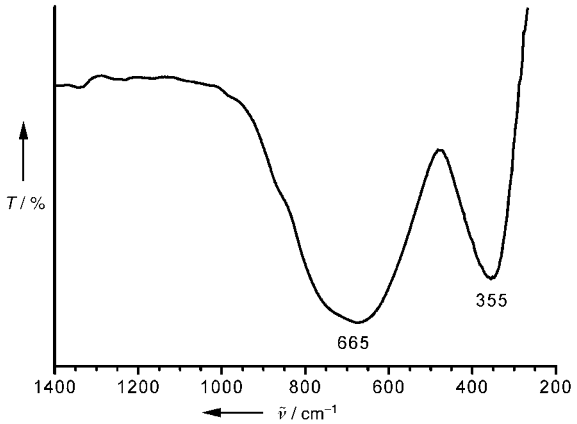


Figure 1. IR spectrum of ABF ($AlBr_{0.13}F_{2.87}$; CsI pellet).

The ^{19}F MAS NMR spectra of ABF, partially fluorinated $AlBr_3$, and ABF exposed to air are given in Figure 2. All spectra show the main signal between $\delta = -160$ and -170 ppm, which is typical for the μ-F atoms of corner-sharing AlF_6 octahedra and is also observed in amorphous and crystalline phases of AlF_3.[3,7] The spectrum of ABF shows an additional weak signal in the region from $\delta = -200$

---

[*] T. Krahl, Prof. Dr. E. Kemnitz
Institut für Chemie
Humboldt-Universität zu Berlin
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
Fax: (+49) 30-2093-7277
E-mail: erhard.kemnitz@chemie.hu-berlin.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (Ke 489/15-1). We thank Dr. J.-D. Grunwaldt and co-workers from the ETH Zurich for performing the EXAFS measurements.

DOI: 10.1002/anie.200460491

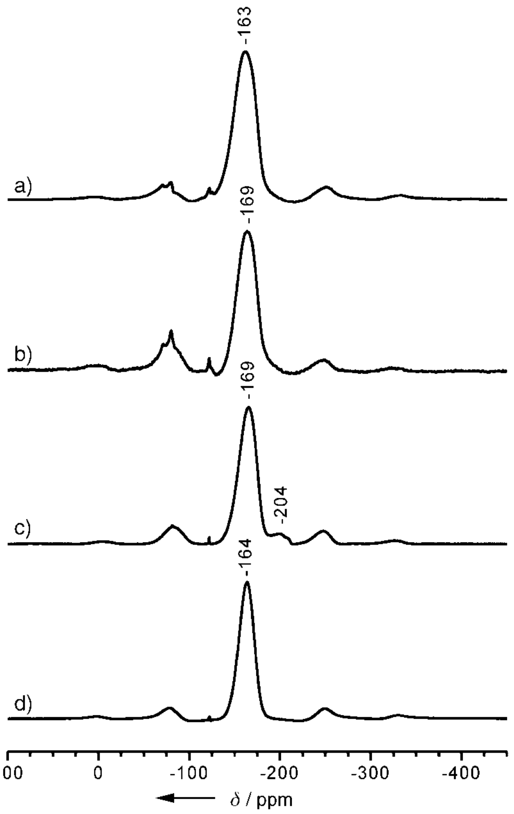


Figure 2. ^{19}F MAS NMR spectra of a) $AlBr_2F$, b) $AlBrF_2$, c) ABF ($AlBr_{0.13}F_{2.87}$), and d) ABF exposed to air for 18 h.

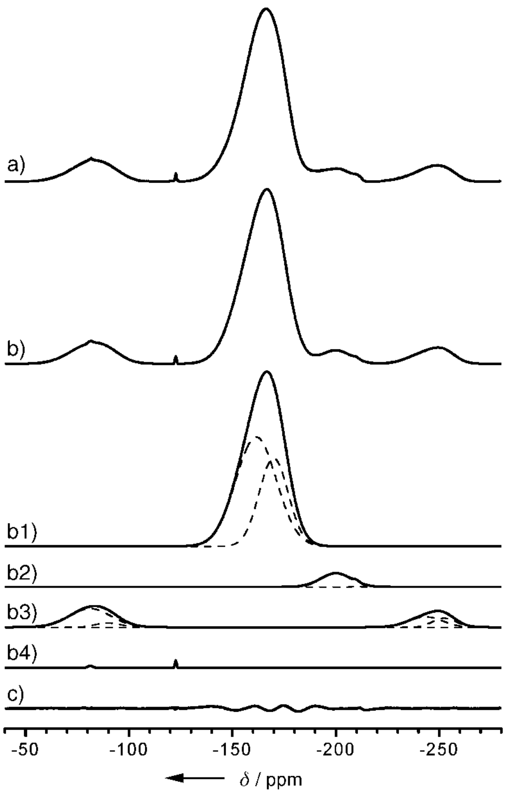


Figure 3. Measured (a) and simulated (b) ^{19}F MAS NMR spectrum of ABF. The fit (b) is the sum of the components (b1) to (b4). The parameters of the lines are shown in Table 1. b1) Main signal, lines 5 and 6; b2) shoulder, lines 7 and 8; b3) spinning side bands, lines 2, 3, 9, and 10; b4) organic residue, lines 1 and 4; c) difference between (a) and (b). The same scale was used for all components.

Table 1: Deconvolution of the ^{19}F MAS NMR spectrum of ABF.[a]

No.	Amplitude [a.u.]	Position [ppm]	Width [kHz]	I_{rel} [%]	Comment
1	1.04	−81.31	1.06	–	organic
2	8.72	−80.18	8.60	–	s.s.b.
3	3.34	−89.80	6.18	–	s.s.b.
4	3.72	−122.64	0.35	–	organic
5	51.30	−161.41	8.89	48.8	bridging fluorine, 92.3 %
6	45.81	−169.84	6.56	43.5	
7	6.75	−200.00	6.02	6.4	terminal fluorine, 7.7 %
8	1.38	−210.00	1.19	1.3	
9	5.33	−243.32	7.34	–	s.s.b.
10	4.56	−252.38	5.15	–	s.s.b.

[a] The parameters of the Gaussian line fit are given. Only the lines 5 to 8 were considered for relative intensity. (I_{rel}) (s.s.b. = spinning side band).

to −210 ppm. According to the superposition model for the ^{19}F chemical shift, this signal is caused by terminal fluorine atoms bound to only one aluminum atom at a distance of around 1.7 Å (t-F).[6a] The appearance of such types of fluorine atoms has only been observed in ACF before and recently also in alumina fluorinated with $CHClF_2$.[7c] Deconvolution of the ^{19}F NMR spectrum of ABF with the program DMFIT[6b] using Gaussian line shapes and two lines for each of the signals shows that the μ-F:t-F ratio of intensities of the fluorine signals is 92.3:7.7 (Figure 3 and Table 1). The small and narrow signals at chemical shifts of about $\delta = -80$ and −120 ppm can be assigned to the CF_3 and CF_2 groups of the organic residue. The signals of the terminal fluorine atoms disappear when the sample is exposed to atmospheric moisture (Figure 2d), and the structure of ABF changes irreversibly.

The fingerprint region of the X-ray absorption near edge spectra (XANES) of the Br K edge of $AlBr_3$, $AlBr_2F$, $AlBrF_2$, and ABF are shown in Figure 4. The spectra of ABF and $AlBr_3$ differ from each other, whereas the spectra of $AlBr_2F$ and $AlBr_3$ are almost the same. The spectrum of $AlBrF_2$ is a superposition of the spectra of $AlBr_3$ and ABF—a linear combination of both data sets delivers the best fit result at 29 % $AlBr_3$ and 71 % ABF. From these results, it is evident that the bromine atoms in ABF and $AlBr_3$ differ from each other—the only partially fluorinated compound $AlBrF_2$ contains two different types of bromine atoms: one similar to the bromine in $AlBr_3$ and another similar to the bromine in ABF. Thus, the measurements confirm that $AlBrF_2$ is a mixture of the two phases, $AlBr_3$ and ABF, and that the remaining bromine in ABF does not derive from unreacted $AlBr_3$.

The FT EXAFS spectra of the Br K edge of $AlBr_3$ and ABF (Figure 5) clearly show that the mean distance between bromine and the surrounding atoms in $AlBr_3$ is smaller than

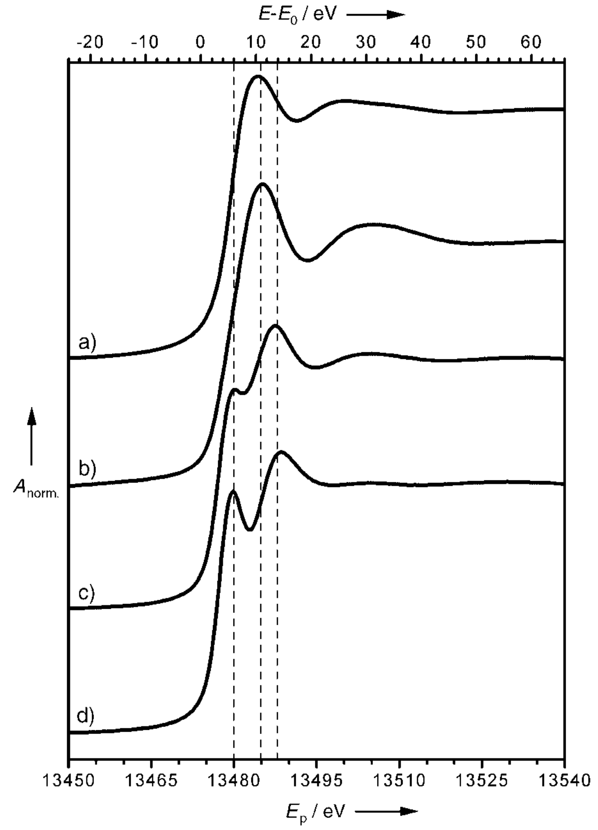


Figure 4. Br K-edge XANES spectra of a) $AlBr_3$, b) $AlBr_2F$, c) $AlBrF_2$, and d) ABF ($AlBr_{0.13}F_{2.87}$). The dashed lines indicate characteristic features. E_P = photon energy.

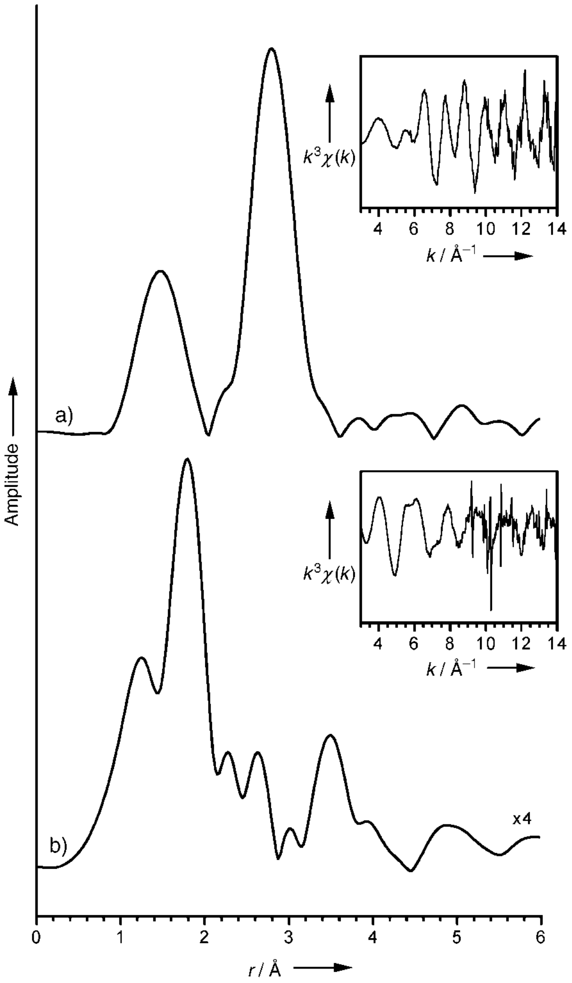


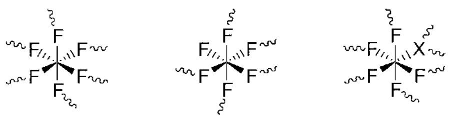
Figure 5. Fourier-transformed EXAFS spectra of the Br K-edge of a) $AlBr_{0.13}F_{2.87}$ (ABF) and b) $AlBr_3$. The transformed spectra are not phase-corrected. The original EXAFS function is shown in the insets.

that found in ABF, that is the Al–Br bonds lengthen during the fluorination. The long Al–Br distances are surprising, but can be explained with the model established in the following.

The results gained from catalysis studies as well as IR and ^{19}F NMR measurements, and thermoanalysis show that the solid phases ABF and ACF are very similar to each other. Nevertheless, there are some spectroscopic methods, which could only be used with one of the phases (EXAFS for ABF, ESR for ACF[3]). The combination of the results of work on ACF[3] and the work on ABF presented here allows us to propose a simple geometric model for the structure of such compounds. It is assumed that ACF and ABF are built up of the same basic units; the structure is explained with a model based on linked polyhedra.

The following assumptions are made:

1) The aluminum atoms are octahedrally coordinated.
2) Three different types of octahedra are present (see Scheme 1):
2a) $[Al(\mu\text{-}F)_{6/2}]^0$ octahedra (**1**), in which all fluorine atoms link two octahedra,
2b) $[Al(\mu\text{-}F)_{5/2}(t\text{-}F)]^{1/2-}$ octahedra (**2**), in which five fluorine atoms link two octahedra and one fluorine atom is terminal,
2c) $[Al(\mu_3\text{-}X)_{1/3}(\mu\text{-}F)_{5/2}]^{1/6+}$ octahedral (**3**), in which one atom X (Cl or Br) links three octahedra and five fluorine atoms link two octahedra.



1 **2** **3**

Scheme 1. Structural octahedral units proposed in ABF and ACF (X = Cl, Br). Al atoms in the middle of the octahedra are not shown. The sinuous lines indicate the bond to the next aluminum atom.

To ensure charge balance, the ratio between **2** and **3** must be 1:3. The overall sum formula can be formulated as $[Al(\mu\text{-}F)_{5/2}(t\text{-}F)]\cdot 3[Al(\mu_3\text{-}X)_{1/3}(\mu\text{-}F)_{5/2}]\cdot n[Al(\mu\text{-}F)_{6/2}]$, where n is a variable parameter. This formula can be simplified to $Al_{4+n}X(t\text{-}F)(\mu\text{-}F)_{10+3n}$. Substitution of n as $\frac{1}{x}-4$ yields $AlX_x(t\text{-}F)_x(\mu\text{-}F)_{3-2x}$, or AlX_xF_{3-x}. For the ABF investigated in this publication n equals 3.69.

This model can explain the ^{19}F NMR and Br K EXAFS spectroscopic data. The following conclusions can be drawn:

1) The formal charge of the octahedra of type **3** is higher than that of the normal octahedra **1** found in AlF_3. Thus, the

electron deficiency of the central Al atom of **3** is higher than that of the Al atoms in AlF_3. Thus, ABF and ACF are more Lewis acidic than AlF_3.

2) From $n \geq 0$ follows $x \leq 0.25$. $AlX_{0.25}F_{2.75}$ is the limiting composition for a compound called "ABF" or "ACF". This agrees quite well with the value 0.3 both given by duPont[2] and determined by ^{19}F NMR spectroscopy for ACF.[3]
3) The ABF structure investigated contains 7.7% terminal fluorine atoms with chemical shifts between $\delta = -200$ and -210 ppm in the ^{19}F NMR spectrum (Table 1). The amount of *t*-F and Br should be the same. Its formula can then be formulated as $AlBr_{0.13}(t\text{-}F)_{0.22}(\mu\text{-}F)_{2.65}$. The amount of *t*-F is a little higher than that of bromine.
4) The mean distance between a μ_3-bridging halogen atom X and aluminum should be comparatively high. The EXAFS spectra (Figure 5) show clearly that the mean distance of bromine to its nearest neighboring atoms is higher in ABF than in crystalline $AlBr_3$—the μ_2-bridging Br atoms have an Al–Br distance of 2.38 Å and the terminal Br atoms have a Al–Br distance of 2.19 to 2.20 Å.[4a]
5) Al–Br bonds are very sensitive to moisture. During exposure to air, not only are the acidic centers on the surface blocked, but the relevant structural elements explained above are destroyed. The resulting compound can be formulated approximately as $Al(OH)_yF_{3-y}$. In the ^{19}F NMR spectrum no signals for terminal fluorine are seen, and the signals are shifted to slightly lower field (Figure 2D). The latter is also observed on comparing the spectra of AlF_3 and $AlF_3{\cdot}3H_2O$.[3]

Experimental Section

Solid-state NMR spectra were measured with a Bruker AVANCE 400 MHz spectrometer equipped with a 2.5-mm Bruker MAS probe head at a rotation frequency of 30 kHz and a resonance frequency of 376 MHz for the ^{19}F nucleus.

Measurements of X-ray absorption spectra were carried out at HASYLAB on the beamline X1 (DESY, Hamburg, Germany) in transmission mode. The edge energy of the Br K-shell (13474 eV) was calibrated with gold foil (Au L_2-edge energy 13733 eV). Samples were mixed with hexagonal boron nitride and pressed into pellets in a dry box.

All preparations were carried out under standard Schlenk conditions. Solvents were dried by condensing over molecular sieves (4 Å) before use. $AlBr_3$ (Reakhim, p.a.), $CFCl_3$ (Fluka, 99.5%), and perfluorooctane (ABCR, 95%) were used for the syntheses. The composition of the samples was checked by Br, C, and F analysis.

Synthesis of ABF: The reaction between $AlBr_3$ and $CFCl_3$ is strongly exothermic and should not be carried out at room temperature. $AlBr_3$ (11.0 g, 41.4 mmol) was placed with a magnetic stirrer in a 250-mL round-bottomed flask equipped with a dry ice condenser. The flask was evacuated and cooled with liquid nitrogen. Six equivalents of $CFCl_3$ (248 mmol) were condensed on the solid. The flask was warmed up to around 200 K (dry ice/2-propanol) and stirred at this temperature for 1 h. The start of the reaction was indicated by the yellow color of the solid. The flask was warmed to room temperature and refluxed for one more hour. The liquid was then evaporated in vacuum, and a fine orange-yellow powder was obtained. The sample had a composition of $AlBr_{0.13}F_{2.87}$ and contained 0.8% carbon.

$AlBr_2F$ and $AlBrF_2$: The reaction was carried out similarly. Perfluorooctane was added until the solid $AlBr_3$ was totally immersed before the reaction. After mixture had been frozen, the desired amount of $CFCl_3$ (for $AlBr_2F$ 1 equiv, for $AlBrF_2$ 2 equiv) was condensed on the solid and then the workup proceeded as described for ABF.

Received: April 28, 2004

Keywords: aluminum · EXAFS spectroscopy · Lewis acids · NMR spectroscopy · structure elucidation

---

[1] a) G. C. Krespan, V. A. Petrov, *Chem. Rev.* **1996**, *96*, 3269–3301; b) C. G. Krespan, D. A. Dixon, *J. Fluorine Chem.* **1996**, *77*, 117–126; c) V. A. Petrov, C. G. Krespan, B. E. Smart, *J. Fluorine Chem.* **1996**, *77*, 139–142; d) V. A. Petrov, C. G. Krespan, B. E. Smart, *J. Fluorine Chem.* **1998**, *89*, 125–130; e) V. A. Petrov, C. G. Krespan, *J. Fluorine Chem.* **2000**, *102*, 199–204.

[2] A. C. Sievert, G. C. Krespan, F. J. Weigert (DuPont Co.), US-A 5.157.171, **1992**.

[3] T. Krahl, R. Stösser, E. Kemnitz, G. Scholz, M. Feist, G. Silly, J.-Y. Buzaré, *Inorg. Chem.* **2003**, *42*, 6474–6483.

[4] a) S. I. Troyanov, *Zh. Neorg. Khim.* **1994**, *39*, 552–555; b) S. I. Troyanov, *Zh. Neorg. Khim.* **1992**, *37*, 266–272.

[5] a) K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *J. Fluorine Chem.* **2000**, *101*, 151–153; b) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, *Inorg. Chem.* **2003**, *42*, 2886–2893.

[6] a) B. Bureau, G. Silly, J.-Y. Buzaré, J. Emery, *Chem. Phys.* **1999**, *249*, 89–104; b) D. Massiot, F. Fayon, M. Kapron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, *Magn. Reson. Chem.* **2002**, *40*, 70–76.

[7] a) P. J. Chupas, M. F. Circoalo, J. C. Hanson, C. P. Grey, *J. Am. Chem. Soc.* **2001**, *123*, 1694–1702; b) J. L. Delattre, P. J. Chupas, C. P. Grey, A. M. Stacy, *J. Am. Chem. Soc.* **2001**, *123*, 5364–5365; c) P. J. Chupas, C. P. Grey, *J. Catal.* **2004**, *224*, 69–79.