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Probing Crystal Structures and Transformation Reactions of Ammonium Molybdates by ^{14}N MAS NMR Spectroscopy

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The unique high-resolution feature offered by ^{14}N magic-angle spinning (MAS) NMR spectroscopy of ammonium ions has been used to characterize the crystal structures of various ammonium molybdates by their ^{14}N quadrupole coupling parameters, i.e., C_Q, the quadrupole coupling constant, and η_Q, the asymmetry parameter. Two polymorphs of diammonium monomolybdate, $(NH_4)_2MoO_4$, recently structurally characterized by single-crystal X-ray diffraction (XRD) and named *m*S60 and *m*P60, show distinct but different ^{14}N MAS NMR spectra from each of which two sets of characteristic ^{14}N C_Q and η_Q values have been obtained. Similarly, the well-characterized ammonium polymolybdates $(NH_4)_2Mo_2O_7$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and $(NH_4)_6Mo_8O_{27}\cdot 4H_2O$ also give rise to distinct and characteristic ^{14}N MAS NMR spectra. In particular, it is noted that simulation of the experimental $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ spectrum requires an iterative fit with six independent NH_4^+ sites. For the slow spinning frequencies employed ($\nu_r = 1500$–3000 Hz), all ^{14}N MAS NMR spectra of the ammonium molybdates in this study are fingerprints of their identity. These different ^{14}N MAS NMR fingerprints are shown to be an efficient tool in qualitative and quantitative assessment of the decomposition of $(NH_4)_2MoO_4$ in humid air. Finally, by a combination of the ^{14}N and ^{95}Mo MAS NMR experiments performed here, it has become clear that a recent report of the ^{95}Mo MAS spectra and data for the *m*S60 and *m*P60 polymorphs of $(NH_4)_2MoO_4$ are erroneous because the sample examined had decomposed to $(NH_4)_2Mo_2O_7$.

1. Introduction

Ammonium molybdates play key roles in the industrial chemistry of molybdenum, either as intermediates or as end-products.[1] Technical grade MoO_3, typically obtained by roasting of MoS_2-containing ores, is purified by extraction with aqueous ammonia, whereby a solution containing MoO_4^{2-} ions is obtained. By large-scale evaporative crystallization such solutions do not give $(NH_4)_2MoO_4$, i.e., the monomolybdate,[2] but rather the dimolybdate $(NH_4)_2Mo_2O_7$, from which pure MoO_3 may be obtained by calcination.[1] $(NH_4)_2Mo_2O_7$ contains anions that are infinite chains of interlinked MoO_4 tetrahedra and MoO_6 octahedra,[3,4] and the compound is insoluble in water. The easily soluble compound $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ is obtained by crystallization from *neutral* aqueous solution and contains a discrete polyanion of seven interlinked MoO_6 octahedra.[5] Particularly, in the older literature, the term "ammonium molybdate" is often used to identify any member of this family of compounds, i.e., no distinction is made between the monomolybdate $(NH_4)_2MoO_4$, the dimolybdate $(NH_4)_2Mo_2O_7$, and the heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. A primary use of these compounds is the manufacture of heterogeneous catalysts for hydrodesulfurization of mineral oil, ammoxidation of propene to acrylonitrile and selective oxidation of methanol to formaldehyde. The ammonium octamolybdate, $(NH_4)_4$-

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Mo_8O_{26}, is used as a smoke- and flame-retarding additive to plastics. In addition to the compounds already mentioned, many more, sometimes poorly characterized, ammonium molybdate materials are known.[6,7] They contain various discrete or polymeric polymolybdate anions. The whole class of compounds has been the subject of extensive studies, and in this context X-ray crystallography[8] and IR and Raman spectroscopy have been particularly useful techniques.[6,7] From an NMR point of view, solid-state ^{95}Mo magic-angle spinning (MAS) and partly also static powder NMR spectroscopy have been extensively applied in the characterization of ammonium and alkylammonium molybdates,[9-14] employing the central transition ($1/2 \leftrightarrow -1/2$) of the ^{95}Mo ($I = 5/2$) quadrupolar nucleus. A recent report has taken advantage of the ultrahigh magnetic fields now available.[15]

In a recent ^{14}N MAS NMR study of ammonium/alkylammonium ions in selected salts, this technique has demonstrated its strong capabilities to determine and characterize the number of different ammonium sites in the asymmetric unit by their ^{14}N quadrupole coupling parameters, i.e., the quadrupole coupling constant (C_Q) and asymmetry parameter (η_Q).[16] These findings prompted an investigation of ammonium molybdates employing ^{14}N MAS NMR as a supplement/alternative to the previously reported ^{95}Mo MAS NMR characterization. Here we report some exciting results from a detailed ^{14}N MAS NMR investigation aimed at characterization of the crystal structures of the most important ammonium molybdates by the ^{14}N quadrupole coupling parameters (C_Q and η_Q). The optimized fitting of simulated to experimental spectra, i.e., the procedure used to obtain these parameters, shows that the distinct features provided by the experimental ^{14}N MAS NMR spectra can actually serve as very convincing fingerprints in the identification of the different ammonium molybdates. In particular, we note that the two polymorphic structures of $(NH_4)_2MoO_4$, recently synthesized and characterized by single-crystal XRD,[2] show distinctively different ^{14}N MAS NMR spectra (fingerprints). Moreover, it will be shown that this fingerprint feature of the ^{14}N MAS NMR spectra can serve as a useful analytical tool in following the well-known[17] decomposition reactions of $(NH_4)_2MoO_4$. These reactions may occur in ordinary humid air where $(NH_4)_2MoO_4$ transforms to $(NH_4)_2Mo_2O_7$ and/or $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, a transformation which can be monitored qualitatively and quantitatively by ^{14}N MAS NMR fingerprints. This is illustrated here for both the *m*S60 and *m*P60 polymorphs of $(NH_4)_2MoO_4$. This decomposition of $(NH_4)_2MoO_4$ appears to be a quite troublesome reaction, judged both from our own experience in the course of this research and from the literature, as will be appropriately discussed during this work. Finally, for some of the ammonium molybdates, a comparison of their ^{14}N MAS NMR fingerprints with the corresponding ^{95}Mo MAS NMR spectra will be performed.

2. Experimental

Materials. Most samples of diammonium monomolybdate, $(NH_4)_2MoO_4$, originate from Aldrich and have been purchased over a period of at least 15 years. The oldest Aldrich sample of $(NH_4)_2MoO_4$ (*mono*-**1**) was purchased about 16 years ago, while two recent samples of $(NH_4)_2MoO_4$ (*mono*-**2** and *mono*-**3**) were purchased just prior to the present study. Attempts have also been made to synthesize both polymorphic structures *m*S60 and *m*P60 of $(NH_4)_2MoO_4$ following the two quite similar procedures recently described.[2] However, in our hands both procedures resulted in the isolation of pure *m*S60 $(NH_4)_2MoO_4$ (*mono*-**4**), as confirmed by the powder XRD pattern. Ammonium dimolybdate and heptamolybdate (i.e., $(NH_4)_2Mo_2O_7$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) were purchased commercially. Hexaammonium octamolybdate, $(NH_4)_6Mo_8O_{27}\cdot 4H_2O$, was obtained as a single pure phase[8] according to powder XRD by stirring a mixture of 31.4 mmol of MoO_3 and 94.3 mmol of $(NH_4)_2Mo_2O_7$ (corresponding to the Mo ratio 1:6) in 100 mL of water at 60 °C for 1 day. All commercial samples were used as received.

^{14}N and ^{95}Mo MAS NMR experiments were performed at 43.33 and 39.09 MHz, respectively, on a Varian Unity INOVA-600 spectrometer equipped with a 14.1 T widebore magnet. A Varian/Chemagnetics broadband low-γ frequency 7.5 mm T3 CP/MAS probe based on transmission-line-tuning technology was used. This probe has a maximum spinning frequency of 7 kHz, and the rotor speed is stabilized to <0.2 Hz using the Varian/Chemagnetics MAS-speed controller. The magic angle of $\theta = 54.736°$ was adjusted to the highest possible precision (i.e., $\Delta\theta < \pm 0.003°$) employing either the ^{14}N MAS NMR spectrum of $Pb(NO_3)_2$[18] or of the ammonium ions for the actual sample. The FWHM (full width at half-maximum) of the spinning sidebands (ssb's) for the ammonium ions can be narrowed down to between 0.45 and 0.60 ppm (i.e., 19 and 25 Hz) during this adjustment for the samples studied. The ^{14}N chemical shifts are referenced to the narrow resonance (FWHM $\approx$ 0.3 ppm) for an external sample of solid NH_4Cl being a primary reference (0 ppm). All other experimental setups were performed as reported elsewhere.[19] Acquisition of the ^{14}N MAS NMR spectra employed single-pulse excitation, a flip angle of ~25°, i.e., $\tau_p = 2$ μs ($\tau_p^{90} = 6.5$ μs), a spectral width of 500 kHz, spinning frequencies mostly of 1500 or 3000 Hz, and a repetition delay usually ranging from 2 to 8 s; however, for $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, a delay of 16 s

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is required. ^{1}H decoupling during acquisition was applied to all spectra recorded for spinning frequencies $\nu_r \leq 3000$ Hz. This narrowed the FWHM of the individual ssb's by ~50% in comparison to the spectrum without decoupling. Because several types of standard low-pass/band-pass filters cause severe intensity distortion in the wings for the spectra of large width as recently shown,[19] ^{1}H decoupling was performed using two homemade in-series 600 MHz traps in the observe line. The ^{95}Mo MAS NMR experiments used spinning frequencies in the range $\nu_r = 2000-6000$ Hz and the spectra are referenced to an external sample of 2.0 M Na_2MoO_4 in water. From the ^{95}Mo MAS NMR experiments performed at the slow spinning frequencies, it was observed that ^{95}Mo CSA values in the range of $\delta_\sigma = -45$ to -80 ppm should be included in the fitting of the experimental spectra. The CSA values are also observed to improve the fit of the manifold of ssb's for the ^{95}Mo satellite ($\pm 3/2 \leftrightarrow \pm 1/2$) transitions.

All spectra were analyzed by computer simulation/iterative fitting on a Sun Microsystem Ultra 5 workstation using the STARS solid-state NMR software package developed in our laboratory and incorporated into the Varian VNMR software.[20] Several new features have been incorporated into the STARS software in order to fully appreciate the effects of many experimental factors associated with ^{14}N MAS NMR, as also recently discussed.[16] In particular, we note that our present version of STARS simultaneously handles up to six different nuclear sites in an iterative fit to the experimental spectrum. The quadrupolar coupling parameters employed in the simulations using STARS are related to the principal elements of the electric-field gradient tensor (**V**) by

$$C_Q = \frac{eQV_{zz}}{h} \tag{1}$$

$$\eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}} \tag{2}$$

where the principal tensor elements are defined by

$$V_{xx} + V_{yy} + V_{zz} = 0 \quad |V_{zz}| \geq |V_{xx}| \geq |V_{yy}| \tag{3}$$

Because of the negligibly small nitrogen CSA apparent from the ^{14}N MAS spectra of the ammonium ions studied here and also observed in the ^{15}N CP/MAS NMR spectra for a few of the samples, i.e., $\delta_\sigma(^{15}\mathrm{N}) = |\delta_{zz} - \delta_{iso}| < 10$ ppm (or the span of the chemical shift tensor $|\Omega| = |\delta_{zz} - \delta_{xx}| < 15$ ppm), the effect of the ^{14}N CSA on the appearance of the ^{14}N MAS NMR spectra can be neglected and has not been considered in the analysis of the spectra.

The ^{95}Mo CSA parameters determined and used by STARS (δ_σ, η_s) are related to the principal elements of the chemical shift tensor by $\delta_\sigma = \delta_{iso} - \delta_{zz}$, $\eta_s = (\delta_{xx} - \delta_{yy})/\delta_\sigma$, $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$ where $|\delta_{zz} - \delta_{iso}| \geq |\delta_{xx} - \delta_{iso}| \geq |\delta_{yy} - \delta_{iso}|$.

3. Results and Discussion

Diammonium Monomolybdate, $(NH_2)_2MoO_4$, *m*S60, and *m*P60 Polymorphs. Quite recent single-crystal XRD studies[2] have shown that $(NH_2)_2MoO_4$ exists in two polymorphic, monoclinic forms, space groups *C*2/*m* (No. 12) and *P*2$_1$/*n* (No. 14). Each of their unit cells contains 60 atoms, and therefore, the two polymorphs have been denoted *m*S60 and *m*P60, respectively.[2] The two structures differ by their lattice constants and in the arrangements of the ammonium ions relative to the MoO_4^{2-} tetrahedra (i.e., different hydrogen-bonding patterns). Since the two polymorphs cannot be distinguished by their IR spectra,[2] it is of interest to investigate the potential possibilities of ^{14}N MAS NMR spectroscopy.[16]

A ^{14}N MAS NMR spectrum of the pure polymorph *m*S60 (*mono*-**4**), synthesized and identified by powder XRD in our laboratories, is shown in Figure 1a. Using our experience from recent ^{14}N MAS NMR studies of ammonium salts, the spectrum has been recorded employing an appropriate slow spinning frequency (i.e., $\nu_r = 1500$ Hz), so as to benefit from the more detailed features exhibited by the envelope of the

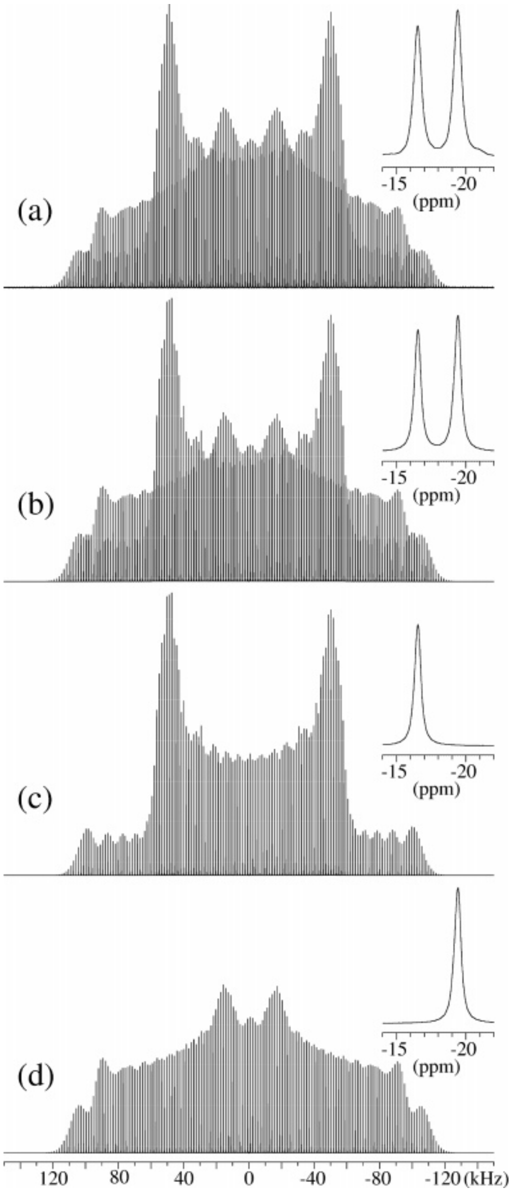

Figure 1. Experimental (a) and simulated (b, c, and d) ^{14}N MAS NMR spectra (43.33 MHz at 14.1 T) of the in-house-synthesized *m*S60 polymorph of $(NH_4)_2MoO_4$ (*mono*-**4**). (a) Experimental spectrum acquired for $\nu_r = 1500$ Hz and 20 000 scans. (b) Simulated spectrum based on the optimized/iteratively fitted parameters for the two NH_4^+ sites (1:0.97) to the experimental spectrum in (a). (c) and (d) Simulated spectra corresponding to the individual parameters for each of the two NH_4^+ sites in Table 1. The insets show expansions of the isotropic resonances for the corresponding spectra.

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Table 1. ^{14}N Isotropic Chemical Shift (δ_{iso}) and Quadrupolar Coupling Parameters (C_Q, η_Q) Determined from ^{14}N MAS NMR of Some Ammonium Molybdates[a]

compound	sites[b]	δ_{iso} (ppm)	C_Q (kHz)	η_Q
$(NH_4)_2MoO_4$ *m*S60	N(1)	−17.4	145.0	0.09
	N(2)	−20.5	152.1	0.72
$(NH_4)_2MoO_4$ *m*P60	N(1)	−22.2	144.4	0.89
	N(2)	−16.6	77.5	0.48
$(NH_4)_2Mo_2O_7$	N(1)	−17.9	251.7	0.91
	N(2)	−16.2	216.5	0.84
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	N(1)	−24.3	122.9	0.92
	N(2)	−14.0	147.7	0.66
	N(3)	−15.8	245.4	0.17
	N(4)	−17.5	145.8	0.90
	N(5)	−24.5	115.8	1.00
	N(6)	−13.6	99.3	0.23
$(NH_4)_6Mo_8O_{27}\cdot 4H_2O$	N(1)	−17.2	129.6	0.57
	N(2)	−16.4	161.6	0.58
	N(3)	−15.8	150.0	0.50

[a] The δ_{iso} values (relative to an external sample of solid NH_4Cl) have an error limit of ±0.1 ppm and include corrections for the second-order quadrupolar shifts, which are in the range of 0.26−3.23 ppm for the samples studied here at 43.33 MHz (14.1T). The C_Q values have error limits better than ±3 kHz and the error limits for η_Q are better than ±0.03. [b] It is noted that the numbering of the nitrogen sites has no relationship to that used for the N atoms used in the reported crystal structures.

ssb intensities at slow spinning speeds.[16] The spectrum shows two well-resolved envelopes of ssb's in accordance with the two crystallographically different NH_4^+ sites of the *m*S60 crystal structure (*C*2/*m*). Combined two-site optimized fitting (STARS) of the ssb intensities for the two ^{14}N manifolds of ssb's leads to the ^{14}N quadrupole coupling (C_Q and η_Q) parameters and δ_{iso} values summarized in Table 1. The simulated spectrum (Figure 1b) corresponding to these parameters shows an excellent agreement with the experimental spectrum (Figure 1a). The simulated spectra corresponding to the individual N(1) and N(2) site are displayed in Figure 1c and d, respectively. It is noted that while the C_Q values for the N(1) and N(2) site are very similar (C_Q = 145.0 and 152.1 kHz, respectively), the asymmetry parameters for these sites differ substantially (η_Q = 0.09 and 0.72, respectively). Although the N−H distances in both polymorphs (*m*S60 and *m*P60), determined from their crystal structures,[2] are associated with large uncertainties, a tentative assignment of the two widely different ^{14}N η_Q parameters for the *m*S60 polymorph to the two crystallographic NH_4^+ sites has been attempted. Inspection of the crystal structures[2] show that the crystallographic N(2) site for the *m*S60 polymorph along with both the N(1) and N(2) sites for *m*P60 (all exhibiting $\eta_Q \geq 0.5$) are located in channels allowing dynamic motions for the NH_4^+ ions. In contrast, the N(1) site for *m*S60 is sandwiched between neighboring MoO_4^{2-} tetrahedra resulting in restricted motion for the N(1) NH_4^+ ions because of a more distinct hydrogen-bonding network. Thus, the NH_4^+ ion exhibiting η_Q = 0.09 in *m*S60 is tentatively assigned to the crystallographic N(1) site.

By recent purchase of a sample of $(NH_4)_2MoO_4$ from Aldrich (*mono*-**2**), it was hoped that this sample would contain at least a mixture (about 1:1) of the *m*S60 and *m*P60 polymorphs as recently observed by other researchers for a $(NH_4)_2MoO_4$ sample purchased from Aldrich and used in a high-field ^{95}Mo MAS NMR investigation.[15] However, powder XRD proved this $(NH_4)_2MoO_4$ sample (*mono*-**2**) to be the pure *m*P60 polymorph. The ^{14}N MAS NMR spectrum of *m*P60 (*mono*-**2**) displays two well-resolved manifolds of ssb's (Figure 2) in agreement with the number of independent NH_4^+ sites in its crystal structure ($P2_1/n$).[2] Since the overall appearances of the ^{14}N MAS NMR envelopes for the manifolds of ssb's for the two polymorphs differ widely, they may, contrary to their IR spectra,[2] serve as distinct fingerprints for the *m*S60 and *m*P60 polymorphs. The ^{14}N C_Q and η_Q values for *m*P60 (Table 1), resulting from two-site iterative fitting of simulated to the experimental ssb intensities (and also used for the simulated spectrum in Figure 2b), clearly reflect the different fingerprints observed in the ^{14}N MAS NMR spectra for *m*S60 and *m*P60. For the N(1) site in *m*P60, the quadrupole coupling parameters (C_Q = 144.4 kHz, η_Q = 0.89) are quite similar to those for the N(2) site in *m*S60, whereas C_Q (=77.5 kHz) for the N(2) site in *m*P60 is by coincidence exactly half the value for C_Q (=145.0 kHz) for the N(1) site in *m*S60. The distinctly different fingerprints for the two *m*S60 and *m*P60 polymorphs of $(NH_4)_2MoO_4$ illustrate that ^{14}N MAS NMR is an effective tool for structural insights to ammonium salts.

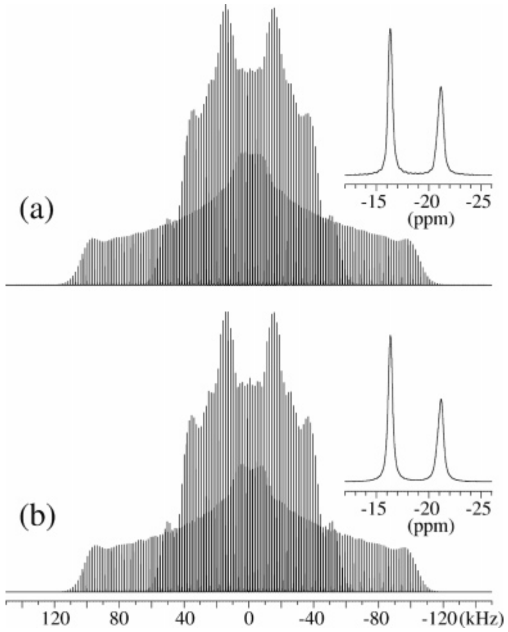

Figure 2. Experimental (a) and simulated (b) ^{14}N MAS NMR spectra (43.33 MHz) of the pure *m*P60 polymorph of $(NH_4)_2MoO_4$ (*mono*-**2**) purchased as $(NH_4)_2MoO_4$ from Aldrich. (a) Experimental spectrum acquired for ν_r = 1500 Hz and 40 000 scans. (b) Simulated spectrum corresponding to the optimized/iteratively fitted parameters (Table 1) for the two NH_4^+ sites (1:1) to the experimental spectrum in (a). The insets show expansions of the isotropic resonances for the corresponding spectra.

Before presenting ^{14}N MAS NMR as a probe in studies of transformation reactions for the two $(NH_4)_2MoO_4$ polymorphs, the ^{14}N MAS NMR results and data obtained for some polynuclear ammonium molybdates will be discussed.

Diammonium Dimolybdate, $(NH_4)_2Mo_2O_7$. The ^{14}N MAS NMR spectrum of $(NH_4)_2Mo_2O_7$ recorded for a spinning frequency ν_r = 1500 Hz shows a manifold of ssb's for which each ssb throughout almost the entire spectrum is partly resolved into two resonances (Figure 3a). A two-site iterative fit to this spectrum gives the optimized quadrupole

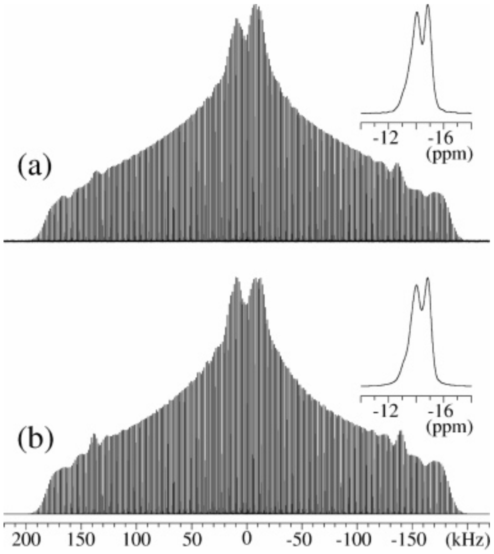

Figure 3. Experimental (a) and simulated (b) ^{14}N MAS NMR spectra (43.33 MHz) of an analytically pure (commercial) sample of diammonium dimolybdate, $(NH_4)_2Mo_2O_7$. (a) Experimental spectrum acquired for $\nu_r = 1500$ Hz and 35 000 scans. (b) Simulated spectrum corresponding to the optimized parameters (Table 1) for the two NH_4^+ sites (1:1). The insets show expansions of the isotropic resonances for the corresponding spectra.

coupling parameters summarized in Table 1 and the corresponding simulated spectrum displayed in Figure 3b. The quadrupole coupling constants for the two NH_4^+ sites are of quite similar magnitude (C_Q = 251.7 and 216.5 kHz) and both larger than the values for the *m*S60 and *m*P60 polymorphs of the monomolybdate. The same statements hold for the corresponding asymmetry parameters which both approach the limit of 1 and altogether indicate quite similar environments for the two NH_4^+ sites. The ^{14}N MAS NMR results are in accordance with the crystal structure reported for $(NH_4)_2Mo_2O_7$.[3,4]

Hexaammonium Heptamolybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. The ^{14}N MAS NMR spectrum of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ obtained for a spinning frequency $\nu_r = 3000$ Hz (Figure 4) shows three resolved resonances for the isotropic peaks in the center of the spectrum and also for most of the ssb's in the manifold of ssb's. The crystal structure determined for $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (monoclinic, space group $P2_1/c$)[5] shows the presence of six different NH_4^+ sites in the asymmetric unit. In order to perform a six-site simulation/iterative fit which encompasses six different NH_4^+ ions within the three resolved manifolds of ssb's, the strategy recently described for a two-site iterative fit to a single ^{14}N manifold of ssb intensities (e.g., for $(CH_3)_3(C_6H_5CH_2)NCl$)[16] has been applied. To ensure reliable intensities for all ssb's in the manifolds and thus a fully relaxed spectrum, it is observed that a relaxation delay of 16 s is required. Integration of all ssb intensities within each of the three manifolds of ssb's shows that the distribution of the six NH_4^+ sites among the three resolved isotropic resonances (Figure 4) should be 2:1:3 in the order from low to high frequency. A simultaneously full six-site iterative fitting to the experimental spectrum, assuming this distribution for the six NH_4^+ sites and for a fixed total intensity of unity for each site, results in the six sets of C_Q, η_Q, and δ_{iso} parameters listed in Table 1. The complete six-site simulated spectrum corresponding to these parameters is shown in Figure 4b and is in excellent agreement with the experimental spectrum. We note that the appearance of the intensities for the expansion of the three resolved isotropic resonances (~3:1:2 from the inset in Figure 4) differs from the overall integrated intensities (2:1:3) for the three manifolds of ssb's because of the difference in the C_Q, η_Q, and δ_{iso} parameters for the six sites. To our knowledge, the ^{14}N MAS NMR spectrum of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ represents the first example for a simultaneous six-site iterative fitting to six partly overlapping manifolds of ssb's.

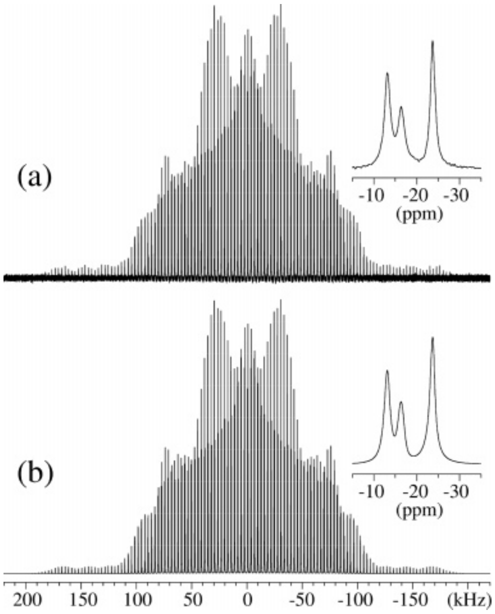

Figure 4. Experimental (a) and simulated (b) ^{14}N MAS NMR spectra (43.33 MHz) of analytically pure hexaammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. (a) Experimental spectrum acquired for $\nu_r = 3000$ Hz, 10 100 scans, and a relaxation delay of 16 s. (b) Simulated spectrum corresponding to the optimized parameters (Table 1) resulting from the six NH_4^+-site iterative fit to the experimental spectrum. The insets show expansions of the resolved isotropic resonances, which correspond to a distribution of 2:1:3 from low to high frequency for the six NH_4^+ sites when the overall integrated intensities of the three resolved manifolds of ssb's are considered.

Hexaammonium Octamolybdate, $(NH_4)_6Mo_8O_{27}{\cdot}4H_2O$. As the last ammonium polymolybdate, we have included $(NH_4)_6Mo_8O_{27}{\cdot}4H_2O$ in this ^{14}N MAS investigation. The ^{14}N MAS NMR spectrum obtained for $\nu_r = 1500$ Hz (Figure 5a) shows two partly resolved manifolds of ssb's with an intensity ratio of 1:2 for the low- to high-frequency manifold, respectively. This also appears in decent agreement with the relative intensities observed for the expansion of the two partly overlapping isotropic resonances shown as an inset in Figure 5. This feature observed for the ^{14}N MAS spectrum is fully consistent with the crystal structure determined for $(NH_4)_6Mo_8O_{27}{\cdot}4H_2O$ (monoclinic, space group $P2_1/c$),[8] which shows the presence of three different NH_4^+ sites in the asymmetric unit. Clearly, this assumes that the high-frequency manifold of ssb's represents two NH_4^+ sites most likely characterized by two different sets of quadrupole coupling parameters. Three-site iterative fitting to the experimental spectrum (one site for the low-frequency and two sites for the high-frequency manifold of ssb's) results

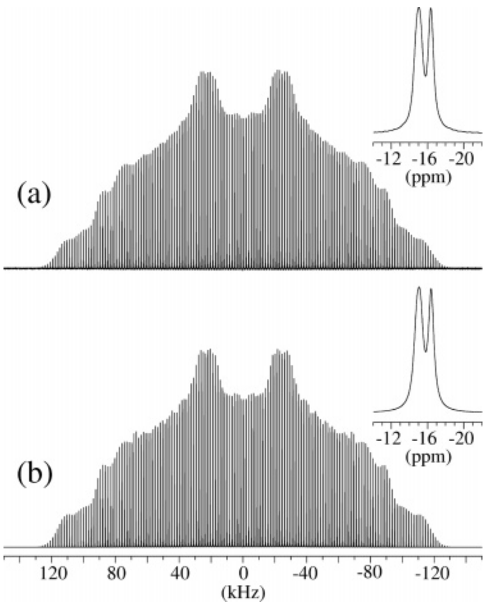

Figure 5. Experimental (a) and simulated (b) ^{14}N MAS NMR spectra (43.33 MHz) of analytically pure hexaammonium octamolybdate, $(NH_4)_6Mo_8O_{27}{\cdot}4H_2O$. (a) Experimental spectrum acquired for $\nu_r = 3000$ Hz and 33 000 scans. (b) Simulated spectrum corresponding to the optimized parameters (Table 1) for the three NH_4^+ sites (1:1:1). The insets show expansions of the two resolved isotropic resonances, for which the resonance at high-frequency corresponds to an overlap of two NH_4^+ sites.

in the three different sets of optimized C_Q, η_Q, and δ_{iso} parameters summarized in Table 1. The complete simulated spectrum (Figure 5b) corresponding to these parameters shows an excellent agreement with the experimental spectrum. The ^{14}N C_Q and η_Q values for the three different NH_4^+ sites are all of quite similar magnitude with only the magnitude of C_Q for the N(1) site being slightly lower (about 20%) than for the two other sites. From the crystal structure of $(NH_4)_6Mo_8O_{27}{\cdot}4H_2O$,[8] it is noted that the NH_4^+ ions along with the water molecules comprise a complex network of hydrogen bonds fixing the layers of distorted MoO_6 octahedra formed by edge and corner sharing.

Transformation Reactions of Diammonium Monomolybdate. As illustrated above, ^{14}N MAS NMR represents a unique tool for characterization of ammonium molybdates through the variation in their ^{14}N quadrupole coupling parameters. The variation in ^{14}N C_Q and η_Q values gives rise to characteristic features for the individual ^{14}N MAS NMR spectra, which serve as useful fingerprints for the ammonium molybdates. This observation became clear to us right from the outset of the present study. When recording the first ^{14}N MAS NMR spectra for a collection of samples from our chemical stockroom, all labeled "$(NH_4)_2MoO_4$" or "ammonium molybdate", it was confusing to observe a series of widely different spectra, i.e., some showing minor "impurity-manifolds of ssb's" in an otherwise well-defined spectrum, and others displaying a well-defined and pure but different spectrum. Further ^{14}N MAS NMR spectra recorded later for samples labeled analytically pure $(NH_4)_2Mo_2O_7$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (and proven as such by powder XRD), appeared to be identical to some of the impurities and well-defined spectra already obtained for the "$(NH_4)_2MoO_4$" stockroom samples. Decomposition of diammonium monomolybdate, $(NH_4)_2MoO_4$, into $(NH_4)_2Mo_2O_7$ and/or $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ is known (e.g., $2(NH_4)_2MoO_4 \rightarrow (NH_4)_2Mo_2O_7 + 2NH_3 + H_2O$). This triggered the synthesis and search (described in the sections above) for pure samples of the recently isolated two *m*S60 and *m*P60 polymorphs of $(NH_4)_2MoO_4$.

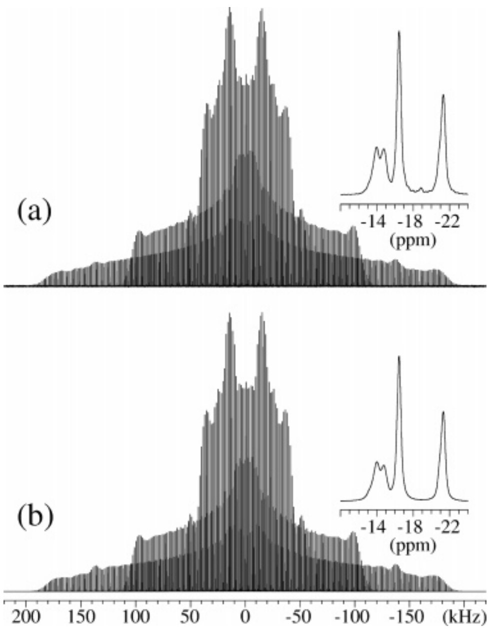

Figure 6. Experimental (a) and simulated (b) ^{14}N MAS NMR spectra (43.33 MHz) of the same sample of $(NH_4)_2MoO_4$ *m*P60 as used in Figure 2 but after exposure to air for 7 days (see text). (a) Experimental spectrum acquired for $\nu_r = 1500$ Hz and 16 000 scans. (b) Simulated spectrum based on a four NH_4^+-site optimization to the experimental spectrum according to two NH_4^+ sites (1:1) for $(NH_4)_2MoO_4$ *m*P60 and two NH_4^+ sites (0.85: 0.85) for $(NH_4)_2Mo_2O_7$. The resulting spectral parameters (C_Q, η_Q, and δ_{iso}) for $(NH_4)_2MoO_4$ *m*P60 and $(NH_4)_2Mo_2O_7$ are within the error limits for the data of the pure samples listed in Table 1.

As a first of several examples encountered during this study on transformation reactions for $(NH_4)_2MoO_4$, the ^{14}N MAS NMR spectrum of a sample of the "as-received" *mono*-**2** *m*P60, which has been exposed to air in an open vial for 7 days, is illustrated in Figure 6. This clearly shows a spectrum composed of ssb manifolds for the *m*P60 polymorph (Figure 2) and for $(NH_4)_2Mo_2O_7$ (Figure 3). Four-site fitting to the experimental spectrum results in the simulated spectrum shown in Figure 6b, and the corresponding spectral parameters are within the error limits shown in Table 1 for $(NH_4)_2MoO_4$, *m*P60, and $(NH_4)_2Mo_2O_7$. The product composition, resulting from the transformation reaction, also follows from the fit in Figure 6b and is ~54 mol % of the *m*P60 polymorph and 46 mol % $(NH_4)_2Mo_2O_7$. Following this experiment, the finely crushed powder packed into the MAS rotor was spread out in a thin layer on a glass surface and left in open air (38% relative humidity) for a further 4 days, when a second/new ^{14}N MAS NMR spectrum of the sample was recorded. This spectrum (Figure 7) shows that a complete transformation of the $(NH_4)_2MoO_4$, *m*P60 polymorph has occurred, resulting in a mixture dominated by $(NH_4)_2Mo_2O_7$ (Figure 3) and to a minor extent $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Figure 4). A quantitative iterative fit of the experimental spectrum in Figure 7a, employing the data for the di- and heptamolybdate in Table 1 and using the

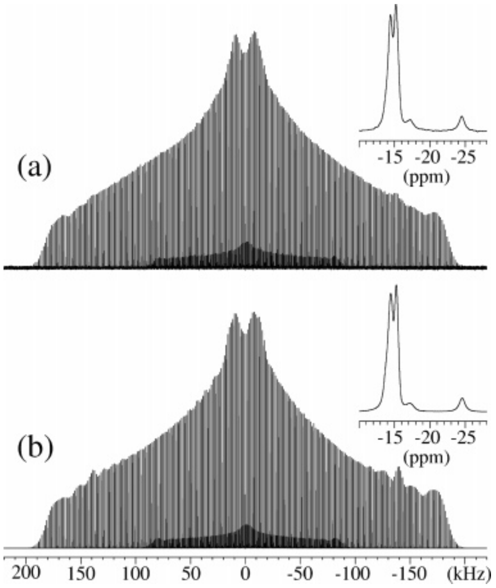

Figure 7. Experimental (a) and simulated (b) ^{14}N MAS NMR spectra (43.33 MHz) of the sample used in Figure 6 but following exposure to air as a thin layer on a glass plate for a further 4 days (see text). (a) Experimental spectrum acquired for $\nu_r = 1500$ Hz and 35 000 scans. (b) Simulation of the spectrum according to a mixture of $(NH_4)_2Mo_2O_7$ and $(NH_4)_6Mo_7O_{24}$·4H_2O using the parameters in Table 1 for the two NH_4^+ sites (1:1) for $(NH_4)_2Mo_2O_7$ and the two NH_4^+ sites at lowest frequency, N(1) and N(5) in Table 1, (0.05:0.05) for $(NH_4)_6Mo_7O_{24}$·4H_2O for the quantitative evaluation of 95 mol % $(NH_4)_2Mo_2O_7$ and 5 mol % $(NH_4)_6Mo_7O_{24}$·4H_2O.

resonance at lowest frequency for $(NH_4)_6Mo_7O_{24}$·4H_2O (corresponding to two NH_4^+ sites) for the quantification, is illustrated in Figure 7b. This shows that under the particular conditions described above the originally pure *m*P60 polymorph has transformed into a mixture of about 95 mol % $(NH_4)_2Mo_2O_7$ and 5 mol % $(NH_4)_6Mo_7O_{24}$·4H_2O.

Regarding the *m*S60 polymorph of $(NH_4)_2MoO_4$, the following examples (spectra not shown) illustrate the transformation reactions observed for this polymorph during this investigation. (i) Following storage of the pure, finely crushed powder of *m*S60 (*mono*-**4**), used to obtain the spectrum in Figure 1, for about 3 months in a small closed container, a new ^{14}N MAS NMR spectrum recorded for this sample showed it to be identical to that for $(NH_4)_2Mo_2O_7$ in Figure 3; this has also been verified by ^{95}Mo MAS NMR (vide infra). (ii) Overnight storage of a pure *m*S60 powder sample on a glass plate in the humid atmosphere (100% relative humidity, 20 °C, closed desiccator), *m*S60 transforms completely into $(NH_4)_2Mo_2O_7$ as seen from the fingerprint ^{14}N MAS NMR spectrum. (iii) The very old $(NH_4)_2MoO_4$ *mono*-**1** sample from Aldrich has been stored in a small closed container in the form of big lumps. Powdering some of this sample followed by recording its ^{14}N MAS spectrum shows *mono*-**1** to be the *m*S60 polymorph with a minor impurity of the dimolybdate $(NH_4)_2Mo_2O_7$ (about 10 mol % from an iterative fit). Therefore, on the basis of our own experience, it is recommended that both polymorphs of $(NH_4)_2MoO_4$ are stored in the smallest possible, tightly closed container under dry air and preferably in the form of large lumps rather than as a fine powder.

The spectra and examples presented in this section clearly demonstrate that the fingerprint ^{14}N MAS NMR spectra of the ammonium mono- and polymolybdates serve extremely useful tools to study, identify, and quantify the transformation reactions and reaction products for the *m*S60 and *m*P60 polymorphs of $(NH_4)_2MoO_4$. However, it is emphasized that the aim of the present investigation has not been a detailed study of these transformation reactions, which seem to be very sensitive to the environmental conditions and which may also differ for the individual two polymorphs under the same conditions. Rather, the purpose has been the presentation of fingerprint ^{14}N MAS NMR spectroscopy as new and efficient tool in such studies.

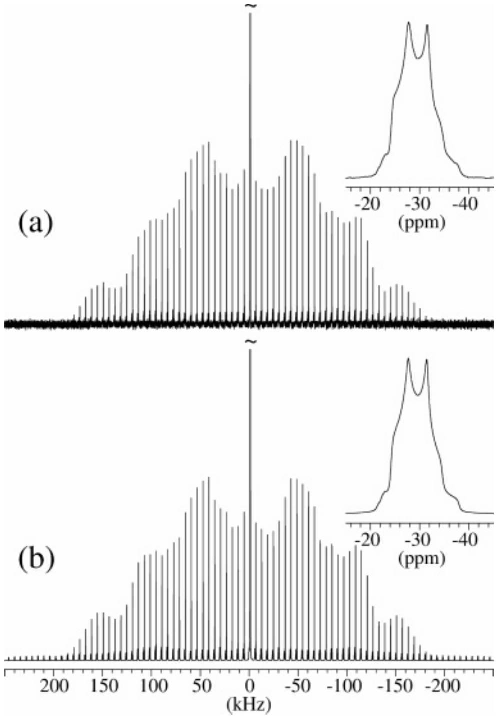

Figure 8. Experimental (a) and simulated (b) ^{95}Mo MAS NMR spectra (39.09 MHz at 14.1 T) of the in-house-synthesized $(NH_4)_2MoO_4$ *m*S60 polymorph (*mono*-**4**). (a) Experimental spectrum of the central and satellite transitions acquired for $\nu_r = 6000$ Hz and 17 000 scans. (b) Simulated spectrum corresponding to the optimized ^{95}Mo C_Q and η_Q parameters in Table 2 and including a chemical shift anisotropy of $\delta_\sigma = -48$ ppm (see text and Table 2). The insets show expansions of the lineshapes for the central transition in the corresponding spectra.

^{95}Mo MAS NMR Spectroscopy. Following the isolation, identification, and characterization by ^{14}N MAS NMR of the *m*S60 and *m*P60 polymorphs of $(NH_4)_2MoO_4$, it is of further interest to characterize these polymorphs by their ^{95}Mo quadrupole coupling parameters employing ^{95}Mo MAS NMR.

The ^{95}Mo MAS NMR spectrum recorded at 14.1 T (39.09 MHz) for the in-house-synthesized and pure *m*S60 polymorph (*mono*-**4**) is shown in Figure 8a and illustrates both the central and almost the complete satellite transition spectrum for this spin $I = 5/2$ nucleus. An optimized and simultaneous fit to these transitions results in the ^{95}Mo C_Q, η_Q, and δ_{iso} values summarized in Table 2 and the simulated spectra shown in Figure 8b. Similarly, a corresponding ^{95}Mo MAS NMR spectrum of the pure *m*P60 polymorph is shown in Figure 9a along with the simulated spectrum (Figure 9b) corresponding to the optimized C_Q, η_Q, and δ_{iso} parameters

Table 2. ^{95}Mo Isotropic Chemical Shift (δ_{iso}), Chemical Shift Anisotropy (δ_σ), and Quadrupole Coupling Parameters (C_Q, η_Q) Determined from ^{95}Mo MAS NMR of Diammonium Monomolybdate (Two Polymorphs) and Dimolybdate[a]

compound	sites	δ_{iso} (ppm)	δ_{sb} (ppm)	C_Q (MHz)	η_Q
$(NH_4)_2MoO_4$ *m*S60		−23.6	−48	1.20 ± 0.02	0.44 ± 0.02
$(NH_4)_2MoO_4$ *m*P60		−26.3	−80	1.45 ± 0.02	0.82 ± 0.02
$(NH_4)_2Mo_2O_7$	Mo(1)	30.2	−[c]	3.12 ± 0.10	0.88 ± 0.04
	Mo(2)	−19.8	−[c]	2.61 ± 0.10	0.32 ± 0.04

[a] The δ_{iso} values (relative to 2.0 M Na_2MoO_4) have an error limit of ±0.5 ppm and include corrections for the second-order quadrupolar shifts, which are in the range from −6.1 to −48.1 ppm for the central transition for the three samples studied here at 39.09 MHz (14.1 T). [b] The δ_σ values are determined from the ssb intensities observed for the central transitions at slow spinning frequencies ($\nu_r = 2000-3000$ Hz) at 39.09 MHz and have an error limit of ±10 ppm. Because of the small δ_σ values, compared to the lower limit for the spinning frequencies required at 39.09 MHz, a value for η_σ could only be determined for the *m*S60 polymorph, i.e., $\eta_\sigma = 0.70 \pm 0.15$. The determined δ_σ values improves the iterative fit for the manifold of ssb's for the observed satellite ($\pm 3/2 \leftrightarrow \pm 1/2$) transitions in Figures 8 and 9. [c] Not determined.

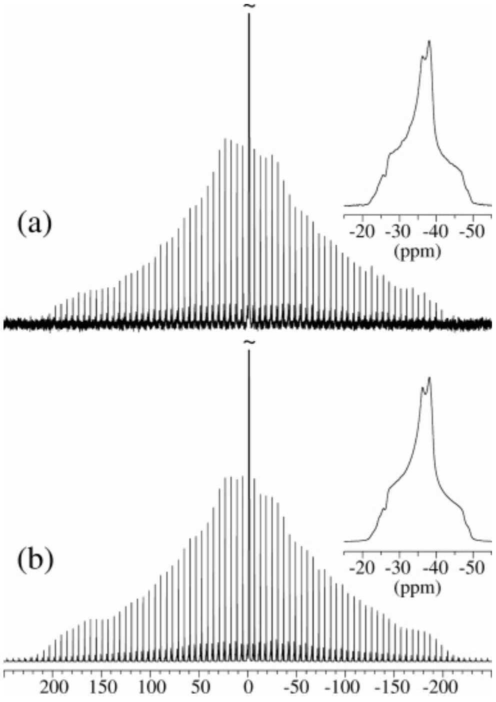

Figure 9. Experimental (a) and simulated (b) ^{95}Mo MAS NMR spectra (39.09 MHz at 14.1 T) of the pure *m*P60 polymorph of $(NH_4)_2MoO_4$ (*mono*-**2**) purchased as $(NH_4)_2MoO_4$ from Aldrich. (a) Experimental spectrum of the central and satellite transitions acquired for $\nu_r = 6000$ Hz and 32 000 scans. (b) Simulated spectrum corresponding to the optimized ^{95}Mo C_Q and η_Q parameters (Table 2) and a chemical shift anisotropy of $\delta_\sigma = -80$ ppm (see text and Table 2). The insets show expansions of the lineshapes for the central transition in the corresponding spectra.

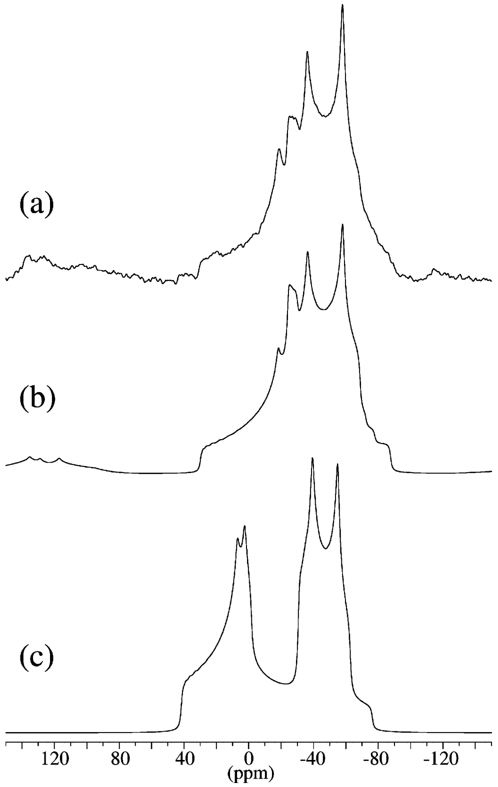

Figure 10. Experimental (a) and simulated (b) ^{95}Mo MAS NMR spectra for the central transition of a commercial, analytically pure sample of $(NH_4)_2Mo_2O_7$ at 39.09 MHz. (a) Experimental spectrum acquired for $\nu_r = 6000$ Hz and 2200 scans. (b) Simulated spectrum corresponding to the optimized parameters in Table 2 for the two Mo sites (1:1) in $(NH_4)_2Mo_2O_7$. (c) Simulated ^{95}Mo MAS NMR spectrum at 54.2 MHz for the central transition using the same parameters as for the simulation in (b) (see text).

given in Table 2. It is noted that the slight asymmetry observed for the intensities within the manifold of ssb's with respect to the central transition for the experimental spectra in both Figures 8 and 9 can be taken care of in the simulations by introducing the ^{95}Mo CSAs determined at slower spinning frequencies, as demonstrated earlier in a ^{95}Mo MAS NMR study of $Mo(CO)_6$.[21] This also improves the rms errors of the fits. Most importantly, it is found that with or without inclusion of ^{95}Mo CSAs in the iterative fitting of these spectra does not influence the values determined for the ^{95}Mo C_Q and η_Q parameters. The quadrupole coupling constants for the $(NH_4)_2MoO_4$ *m*S60 and *m*P60 polymorphs ($C_Q = 1.20$ and 1.45 MHz, respectively) are of quite similar magnitude but very much smaller than the values $C_Q = 2.6$ and 3.21 MHz, respectively, recently determined from a high-field (19.6 T, 54.2 MHz) ^{95}Mo MAS NMR spectrum of a sample reported to be a mixture of the *m*S60 and *m*P60 polymorphs[15] (in an approximate 1:1 ratio estimated from the published spectrum). Considering the transformation reactions, described and observed above from the fingerprint ^{14}N MAS NMR spectra, for $(NH_4)_2MoO_4$ decomposing into $(NH_4)_2Mo_2O_7$ or a mixture of $(NH_4)_2Mo_2O_7$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, it was decided to record the ^{95}Mo MAS NMR spectrum for the pure commercial sample of $(NH_4)_2Mo_2O_7$ and for one of our *m*S60 $(NH_4)_2MoO_4$ samples that has transformed completely into $(NH_4)_2Mo_2O_7$ (vide supra). The 39.09 MHz ^{95}Mo MAS NMR spectrum of the central transition for the commercial $(NH_4)_2Mo_2O_7$ sample is displayed in Figure 10a. The spectrum for the product resulting from the transformation of *m*S60 is exactly identical and is not shown. STARS fitting of the spectrum in Figure 10a requires two different molybdenum sites, which is in accordance with the reported crystal structure for $(NH_4)_2Mo_2O_7$.[3,4] The two sets of optimized ^{95}Mo C_Q, η_Q, and δ_{iso} values for $(NH_4)_2Mo_2O_7$ are summarized in Table 2, and the

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(21) Vosegaard, T.; Skibsted, J.; Jakobsen, H. J. *J. Phys. Chem. A* **1999**, *103*, 9144−9149.

corresponding simulated spectrum is shown in Figure 10b. The two sets of ^{95}Mo quadrupole coupling parameters are very similar to those determined from the high-field (54.2 MHz) ^{95}Mo MAS NMR study of the "quoted" mixture of *m*S60 and *m*P60 polymorphs. Indeed, using the ^{95}Mo data determined in this study for $(NH_4)_2Mo_2O_7$ (Table 2) in a simulation of the appearance for the ^{95}Mo MAS NMR spectrum observed at 54.2 MHz gives a spectrum (Figure 10c) very similar to that for the "claimed" *m*S60 and *m*P60 mixture of polymorphs and published in ref 15. Thus, it is without doubt that the author's original commercial sample of $(NH_4)_2MoO_4$ had transformed into $(NH_4)_2Mo_2O_7$ before their ^{95}Mo MAS NMR spectrum had been recorded.

4. Conclusions

^{14}N MAS NMR spectroscopy applied to ammonium ions at the slow and stable spinning frequencies in the range $\nu_r = 1500-3000$ Hz is shown to be a unique method for structural characterization of various ammonium molybdates. The two polymorphs *m*S60 and *m*P60 of $(NH_4)_2MoO_4$, recently synthesized and structurally characterized by single-crystal XRD, are easily distinguished by their ^{14}N MAS NMR spectra which can be used as fingerprints of their crystal structures. This also holds for the ammonium polymolybdates investigated here. These ^{14}N MAS NMR fingerprints are an efficient tool in studies of the decomposition for the two polymorphs of $(NH_4)_2MoO_4$ both qualitatively and quantitatively. It is noted that the appearances of these ^{14}N ssb manifolds are generally independent of the magnetic field strength employed for the acquisition of the spectra, which emphasize their use as fingerprints.

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