Advancements in natural abundance solid-state ^{33}S MAS NMR: characterization of transition-metal M=S bonds in ammonium tetrathiometallates†

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We report the first ^{33}S chemical shift anisotropy (CSA) data as obtained from a combined determination of ^{33}S CSA and quadrupole coupling parameters utilizing the observation of both the ^{33}S ($I = 3/2$) central and satellite transitions in a natural abundance ^{33}S MAS NMR study aimed at characterizing the two important tetrathiometallates $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$.

Natural abundance ^{33}S NMR of solids has been very little explored because of the difficulties associated with the very low natural abundance (0.76%) and low-γ for the ^{33}S ($I = 3/2$) spin isotope. Early and recent solid-state ^{33}S NMR investigations include static or MAS studies of the central transition in some inorganic compounds, in particular sulfates.[1] As a first significant step towards a more general use of solid-state ^{33}S NMR, this communication reports on the acquisition and analysis of some unique and complete natural abundance ^{33}S MAS NMR spectra (i.e., the central (1/2 ↔ −1/2) as well as the satellite (±3/2 ↔ ±1/2) transitions) for characterization of two transition-metal tetrathiometallates, $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$ which , e.g., serve as precursors for catalytically active metal sulfides. Fairly small quadrupole coupling constants are expected for these compounds based on the narrow ^{33}S resonances observed for their solution-state spectra.[2] Recent experiences gained from our continuous advancements of solid-state ^{14}N ($I = 1$) MAS NMR[3] have been brought into full advantage, since ^{14}N and ^{33}S are neighbors in the low-frequency end of the NMR-frequency table; only 3 MHz apart at 14.1 T.

Transition-metal sulfide structures constitute key catalytic reaction centers in both molecular biology and chemical industry.[4] For example, heterogeneous Co–MoS$_2$ and Ni–MoS$_2$ hydrodesulfurization (HDS) catalysts[5] are used extensively in oil refineries. Ammonium thiometallates, $(NH_4)_2MS_4$ (M = Mo, W), may act as single source precursors of MS_{2+x} ($0 \leqslant x \leqslant 1$) nanoparticles by simple thermal decomposition[6] while molecular metal-sulfide clusters derived from $[MS_4]^{2-}$ provide molecular-level insight into the mechanism of HDS.[7] Outside the area of catalysis, the semiconductivity of MoS$_2$ and WS$_2$ opens for

promising applications.[8a,b] Within medicine, $(NH_4)_2MS_4$ compounds are used in the treatment of several diseases including breast cancer, hepatitis, and the copper metabolism disorder known as Wilson's disease.[8c]

The isostructural diammonium tetrathiomolybdate $((NH_4)_2MoS_4)$[9a] and tetrathiotungstate $((NH_4)_2WS_4)$[9b] crystallize in the orthorhombic space group *Pnma* ($Z = 4$). All the tetrathiometallate anions, $[MS_4]^{2-}$ (M = Mo, W), are equivalent but each exhibits three crystallographically independent S sites, i.e., two out of the four S atoms in the $[MS_4]^{2-}$ ion are equivalent. The complete natural abundance ^{33}S MAS NMR spectrum (14.1 T, 46.04 MHz) of $(NH_4)_2WS_4$, shown in Fig. 1(a) for a spinning frequency $v_r = 6.0$ kHz, is fully consistent with this crystal structure. The ^{33}S central transition in this spectrum displays the typical appearance of a pseudo-spin-1/2 nucleus being influenced by the interaction of chemical shift anisotropy (CSA) in that it is split into a group of about six spinning sidebands (ssbs) separated by 6 kHz. Moreover, each of these groups of ssbs consists of three resonances with an intensity ratio of approximately 2 : 1 : 1 (from high to low frequency), and with the individual resonances displaying lineshapes, which are caused by the second-order quadrupolar broadening combined with the angular dependencies of the quadrupole and CSA tensorial interactions.[10] This is most clearly illustrated by the expansion for the central transition in Fig. 2(a). In addition to the central transition, the ^{33}S satellite transition spectrum (Fig. 1(a)) has been used to full advantage for the determination of the quadrupole coupling constants (C_Q) and asymmetry parameters (η_Q) for the three different ^{33}S sites. It is obvious that the distinct detection of the satellite transitions for all three resolved sites reported here has been a prerequisite for determination of precise C_Q, η_Q values. This would have been impossible solely based on the very small effects of the second-order quadrupole interactions on the lineshapes (Fig. 2). A final combined and simultaneous three-site optimized fitting of these three manifolds of ssbs involving both the central and satellite transitions, using the STARS program,[3,10] results in the ^{33}S C_Q, η_Q, and CSA (δ_{iso}, δ_σ, η_σ) values summarized in Table 1 for the three independent S sites of $(NH_4)_2WS_4$. Also the three Euler angles (ψ, χ, ξ) describing the relative orientation of the quadrupole coupling and chemical shift tensors, as defined elsewhere,[10] influence the spectrum in Fig. 1(a) and have been determined. However, it has not been possible to extract any new structural information from these Euler angles because of their large error limits (see ESI†). The complete simulated spectrum in Fig. 1(b), which corresponds to the data in Table 1, shows an excellent agreement with the experimental spectrum, as can also be

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† Electronic supplementary information (ESI) available: Experimental details. Synthesis and ^{33}S MAS NMR spectroscopy of $(NH_4)_2MS_4$ (M = Mo, W). See DOI: 10.1039/b618497a
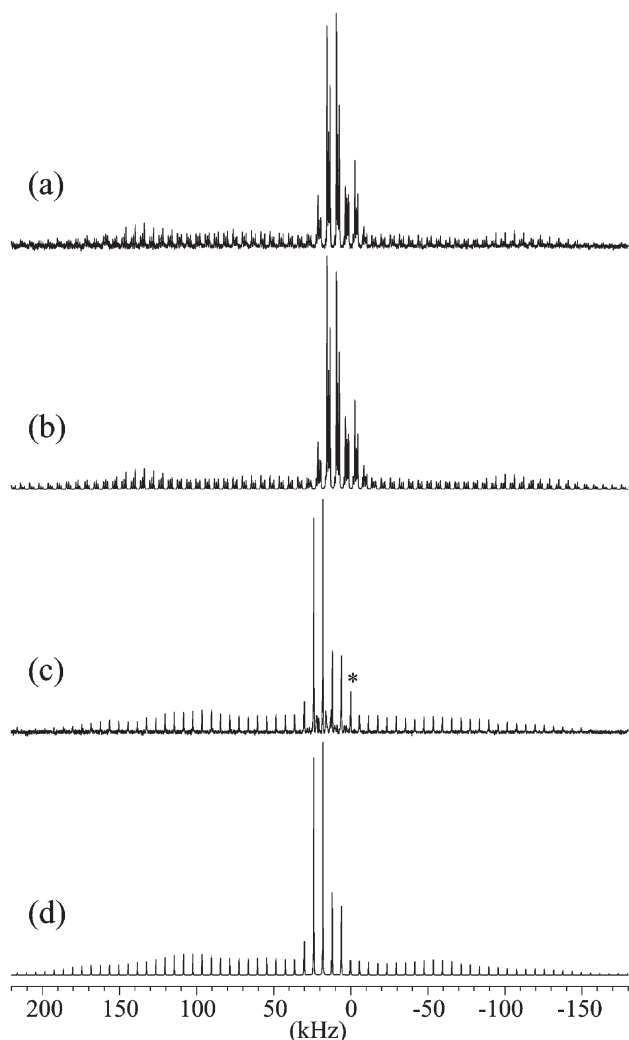
Fig. 1 Experimental (a, c) and simulated (b, d) natural abundance ^{33}S MAS NMR spectra of $(NH_4)_2WS_4$ (a, b) and $(NH_4)_2MoS_4$ (c, d).
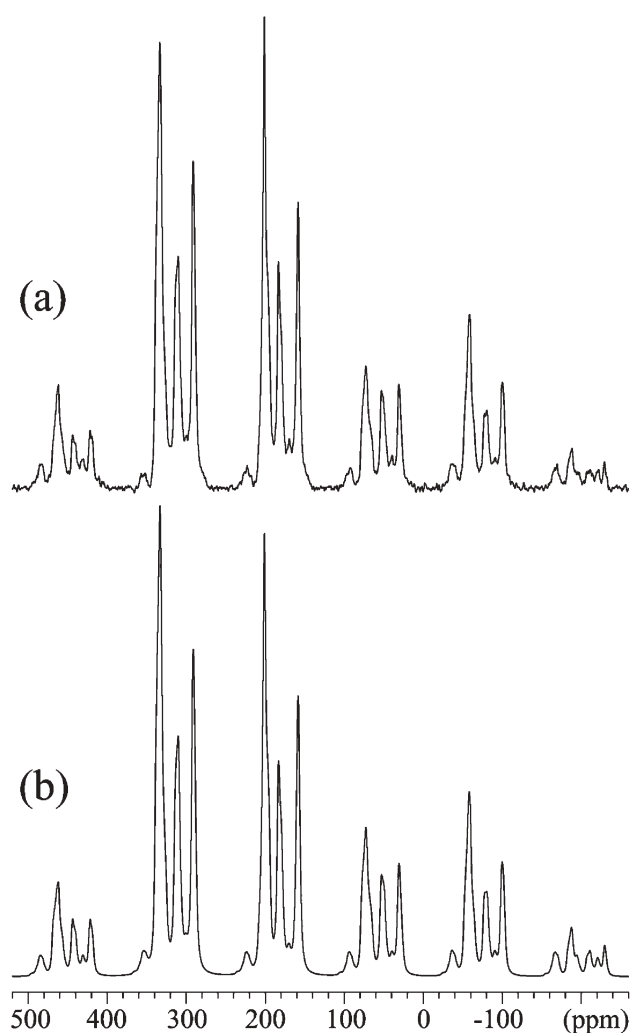

Fig. 2 Expansions for the central transitions in the experimental and simulated ^{33}S MAS NMR spectra of $(NH_4)_2WS_4$ in Fig. 1(a) and (b).

judged from the expansions of the central transitions in Fig. 2. The ^{33}S CSA data in Table 1 are the first reported for ^{33}S in any sulfur compound. Finally, we note from simulations based on the same data that some of the ssbs for the satellite transitions display lineshapes that require inclusion of the effect from the second-order quadrupolar-CSA cross-term in the average Hamiltonian, an effect recently observed experimentally for the first time in ^{14}N MAS NMR[3] and incorporated as an option into STARS.

The natural abundance ^{33}S MAS NMR spectrum for the isostructural tetrathiomolybdate compound $(NH_4)_2MoS_4$ is shown in Fig. 1(c), also for $\nu_r = 6.0$ kHz. This spectrum differs from that for $(NH_4)_2WS_4$ in that the three different ^{33}S resonances, representing the three different S-sites in $(NH_4)_2MS_4$, are here averaged into a single set of narrow resonances for the ssbs of the central and satellite transitions. Analysis of the spectrum by STARS fitting of the ssb intensities for the central and satellite transitions yields the averaged spectral parameters summarized in Table 1 and the corresponding simulated spectrum in Fig. 1(d). It is seen that the magnitude of the anisotropic parameters (C_Q, δ_σ) determined for $(NH_4)_2MoS_4$ are all slightly smaller than the values for each of the three different S sites in $(NH_4)_2WS_4$. The reason for

Table 1 ^{33}S Quadrupole coupling (C_Q, η_Q) and chemical shift parameters (δ_σ, η_σ, δ_{iso}) for $(NH_4)_2MS_4$ (M = W, Mo) from natural abundance ^{33}S MAS NMR spectra[a]

Compound/sites	C_Q/kHz	η_Q	δ_σ (ppm)	η_σ	δ_{iso} (ppm)
$(NH_4)_2WS_4$					
S(1), S(2)	708	0.77	389	0.16	209.3
S(3)	620	0.14	396	0.35	185.7
S(4)	531	0.08	380	0.05	162.9
$(NH_4)_2MoS_4$					
S (av.)	520	0.35	347	0.15	393.0

[a] The δ_{iso} values (relative to 1.0 M Cs_2SO_4) have an error limit of ± 0.3 ppm. The error limits for C_Q, η_Q, δ_σ and η_σ are ± 5 kHz, ± 0.05, ± 3 ppm and ± 0.05, respectively.

the averaging of the ^{33}S resonances in the $[MS_4]^{2-}$ moiety of $(NH_4)_2MoS_4$ as opposed to $(NH_4)_2WS_4$ could be related to the stronger N–H⋯S=M hydrogen bonding network in $(NH_4)_2WS_4$[11] as compared to $(NH_4)_2MoS_4$.[12] Thus, no disordering of the H atoms in the NH_4^+ ions is observed for $(NH_4)_2WS_4$[11] while the H atoms are disordered over two orientations for both NH_4^+ ions in $(NH_4)_2MoS_4$.[12] Clearly this could lead to a difference in the motional averaging for the three crystallographically independent

S-sites for the two isostructural $(NH_4)_2MS_4$ thiometallates. This becomes reflected on the timescale for averaging of the fairly small chemical shift differences (Table 1) in their ^{33}S MAS NMR spectra at ambient temperature (for v_r = 6.0 kHz this corresponds to 38 °C[1d]). The different appearances for the MAS NMR spectra (Fig. 1) of the two isostructural thiometallates illustrate that solid-state ^{33}S MAS NMR can supplement and provide additional structural information to that obtained from X-ray diffraction.

The present work intends to illustrate the potential of "state-of-the-art" solid-state ^{33}S MAS NMR to metal-sulfide heterogeneous catalysts in particular, and to chemistry in general. This technique has so far been considered very difficult and has thus been neglected, primarily as a result of the low natural abundance and low-γ for ^{33}S. The unique natural abundance ^{33}S MAS NMR spectra, including both the central and satellite transitions, presented here for two ammonium tetrathiometallates should serve as an appetizer to focus on potential applications of this technique within the multitude areas of chemistry.

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