

**Advancements in natural abundance solid-state ^{33}S MAS NMR:
Characterization of transition-metal M=S bonds in ammonium tetrathiomallates**

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Experimental details

Materials. $(\text{NH}_4)_2\text{MoS}_4$ was obtained as maroon crystals when a solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in aqueous ammonia was saturated with gaseous hydrogen sulfide.¹ Anal. Calcd. for $\text{H}_8\text{MoN}_2\text{S}_4$: N, 10.7. Found: N, 10.2. Identity was confirmed by X-ray powder diffraction (PDF# 48-1662). $(\text{NH}_4)_2\text{WS}_4$ was obtained as yellow crystals by a procedure similar to that of $(\text{NH}_4)_2\text{MoS}_4$. H_2WO_4 was dissolved in aqueous ammonia. Calcd. for $\text{H}_8\text{WN}_2\text{S}_4$: N, 8.0. Found: N, 7.6. Identity was confirmed by X-ray powder diffraction (PDF# 48-1663).

NMR Spectroscopy. The ^{33}S MAS NMR experiments were performed at 46.04 MHz (14.1 T) on a Varian *Unity* INOVA-600 spectrometer equipped with a 14.1 T widebore magnet and employing a Varian/Chemagnetics 7.5 mm T3[®] CP/MAS probe. The spinning frequency $\nu_r = 6000$ Hz for the 7.5 mm rotors was stabilized to ≤ 1 Hz using a Chemagnetics MAS-speed controller. The magic angle of $\theta = 54.736^\circ$ was adjusted to the highest possible precision ($< \pm 0.005$) by performing ^{14}N MAS NMR (43.34 MHz) on a sample of $(\text{CH}_3)_4\text{NI}$ or $\text{Pb}(\text{NO}_3)_2$ according to the procedure described elsewhere.² The ^{33}S MAS NMR spectra employed single-pulse excitation, a flip angle about 30° (i.e., $\tau_p = 2 \mu\text{s}$ for $\tau_p^{90}(\text{liquid}) = 6.3 \mu\text{s}$) or $\gamma B_1/2\pi = 40$ kHz), a spectral width of 0.5 MHz, and a relaxation delay of 1 s for both samples. The experimental spectrum for $(\text{NH}_4)_2\text{WS}_4$ in Figure 1a

required 316000 scans and that for $(\text{NH}_4)_2\text{MoS}_4$ in Figure 1c 182000 scans. The pulse-width calibration employed an external sample of 1.0 M aqueous Cs_2SO_4 which was also used as a secondary ^{33}S chemical shift reference (333 ppm relative to CS_2). The δ_{iso} values (Table 1) include corrections for the second-order quadrupolar shifts, which are in the range -3.3 ppm to -7.1 ppm for the two samples studied at 46.04 MHz (14.1 T). All spectra were analyzed by simulation/iterative fitting on a Sun Microsystems Ultra-5 workstation using the STARS solid-state NMR software incorporated into the Varian VNMR software. The simulated spectra (Figure 1b and 1d), shown below the corresponding experimental spectra, used the data in Table 1, the Euler angles presented below, and a rf offset of 70 kHz (ascribed to non-ideal cable lengths). In addition the simulation in Figure 1b employed a small deviation ($\Delta\theta = 0.015^\circ$) from exact magic-angle setting. Minor "impurity" resonances are observed in the experimental spectrum in Figure 1c.

Euler Angles. The definition of the quadrupole coupling and chemical shift parameters along with the relative orientation of their respective two tensors (described by the ψ , χ , ζ Euler angles) follow the convention given elsewhere.³ The ψ , χ , ζ Euler angles have been obtained from the optimized fitting for the individual S-sites. For $(\text{NH}_4)_2\text{WS}_4$, S(1), S(2): $\psi = 150^\circ$, $\chi = 10^\circ$, $\zeta = 0^\circ$; S(3): $\psi = 90^\circ$, $\chi = 47^\circ$, $\zeta = 75^\circ$; S(4): $\psi = 50^\circ$, $\chi = 5^\circ$, $\zeta = 15^\circ$. For $(\text{NH}_4)_2\text{MoS}_4$, S(av): $\psi = 0^\circ$, $\chi = 30^\circ$, $\zeta = 0^\circ$. The smallest error limits for these Euler angles are observed for the χ angle and are about $\pm 20\%$, whereas the error limits for the ψ and ζ angles are much higher and could even be undefined for small values of η_Q and η_σ .

References

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