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Site Preferences of NH_4^+ in Its Solid Solutions with Cs_2WS_4 and Rb_2WS_4 from Multinuclear Solid-State MAS NMR

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Solid solutions of NH_4^+ in Cs_2WS_4 and Rb_2WS_4 are obtained by precipitation/crystallization from aqueous solutions. By means of ^{14}N, ^{87}Rb, and ^{133}Cs magic angle spinning NMR, compositions and extraordinarily accurate NH_4^+-site preferences are established for these materials.

Ammonium and alkali metal tetrathiotungstates and -molybdates (A_2MS_4, A = NH_4, Rb, Cs, and M = W, Mo) have been synthesized[1−3] and characterized[1,4,5] by various methods and have attracted interest in many areas of interdisciplinary research,[6] for example, heterogeneous catalysis;[7−9] semiconductors;[10] and the treatment of different diseases including breast cancer, hepatitis, and Wilson's disease.[11] Cs_2WS_4 and Rb_2WS_4 can be synthesized by alkali metal-ion addition to aqueous solutions of $(NH_4)_2WS_4$, where one set of samples is obtained by fast precipitation (in concentrated solutions), whereas the other set is obtained by slow crystal growth (from dilute solutions). Chemical analyses show the presence of minor nitrogen (N) impurities in most of the samples and show that the N content differs not only between the Cs_2WS_4 and Rb_2WS_4 samples but also between the two Cs_2WS_4 and the two Rb_2WS_4 samples prepared by slightly different methods. Thus, a *lower* N content is always observed for Cs_2WS_4 as compared to Rb_2WS_4; however, the N content is *higher* in both Cs_2WS_4 and Rb_2WS_4 when synthesized by fast precipitation rather than by slow crystal growth. To explore these observations and to understand the nature of the nitrogen content, that is, possibilities of either impurities of NH_4^+ salt(s) or solid solutions of NH_4^+ ions in the alkali metal tetrathio-tungstates, a solid-state ^{14}N, ^{133}Cs, and ^{87}Rb magic angle spinning (MAS) NMR investigation has been carried out. In this way, isomorphous substitution of NH_4^+ ions into the alkali metal-ion sites of Cs_2WS_4 and Rb_2WS_4 has been demonstrated for the first time. It is particularly interesting that MAS NMR allows a determination with high precision of site preferences for the NH_4^+ ions between the two crystallographically different alkali metal-ion sites in the isomorphous Cs_2WS_4 and Rb_2WS_4 *Pnma* structures. These NMR results are the first of their kind and are obtained with a precision that far exceeds that obtainable by other techniques (e.g., X-ray diffraction, XRD).

Both preparative methods employed in this study involve stoichiometric mixing of aqueous solutions of $(NH_4)_2WS_4$ and Cs^+ (or Rb^+) salts, resulting in the precipitation of crystalline Cs_2WS_4 (or Rb_2WS_4). The only difference is that, by one method (C), Concentrated solutions ($[WS_4^{2-}] = 0.25$ mol/L) are used, whereas by the other method (D), Dilute

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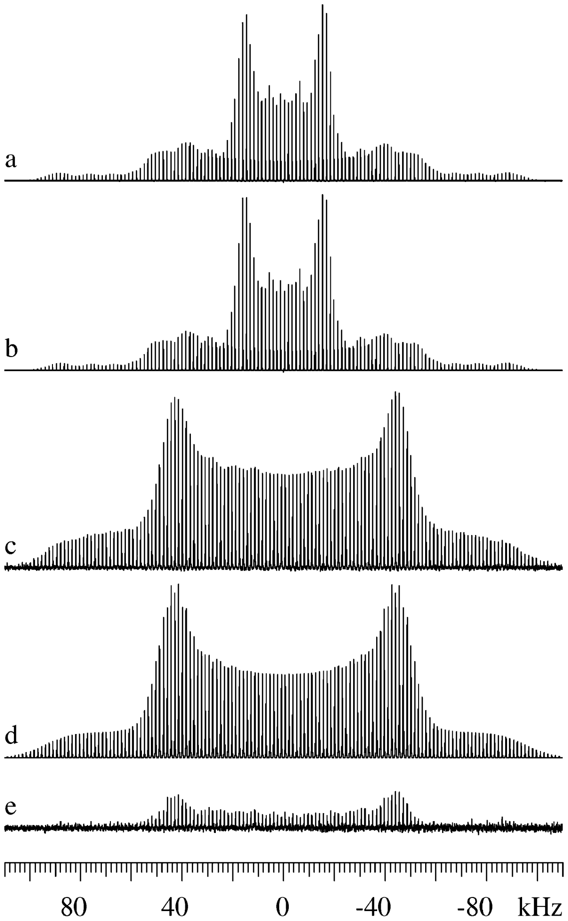

Figure 1. ^{14}N MAS NMR spectra obtained at 43.34 MHz (14.1 T) and for $\nu_r = 1500$ Hz. (a) Experimental (31 000 scans, 17.2 h) and (b) simulated spectra for $(NH_4)_2WS_4$. (c) Experimental spectrum of Cs_2WS_4(C) (118 000 scans, 2.7 days) and (d) the corresponding simulated spectrum obtained for a Gaussian distribution of C_Q and η_Q (see main text). (e) Experimental spectrum of Cs_2WS_4(D) shown on the same absolute intensity scale as the spectrum in c. The intensity ratio between the spectra in c and e is 5.4:1.

solutions ($[WS_4^{2-}] = 0.005$ mol/L) are used. It is noted that method D has been employed for the preparation of crystals of Cs_2WS_4 recently used for determination of its crystal structure by single-crystal XRD.[3]

In the direct observation of the ^{14}N MAS NMR spectra, we have taken advantage of the improved techniques developed for this nucleus during recent years in our laboratory.[12] Experimental ^{14}N MAS NMR spectra of $(NH_4)_2WS_4$, Cs_2WS_4(C), and Cs_2WS_4(D) are shown in Figure 1a,c,e (note: (C) and (D) after the formulas refer to the methods of preparation, vide supra). The optimum fitted/simulated spectra for $(NH_4)_2WS_4$ and Cs_2WS_4(C) are shown in Figure 1b and d and the corresponding spectral parameters summarized in Table 1. Clearly, the spectrum of $(NH_4)_2WS_4$ shows two overlapping manifolds of spinning sidebands (ssb's), in accordance with the crystal structure:[13] one with a "large" (129 kHz) and the other a with "small" (48 kHz) C_Q value. In contrast, the ^{14}N MAS NMR spectrum of Cs_2WS_4(C) (118 000 scans, 2.7 days) in Figure 1c displays only a single manifold of ssb's and with no indication of the presence of a second manifold. Thus, this spectrum indicates the presence of only a single NH_4^+ site in Cs_2WS_4(C) having a $C_Q(^{14}N)$ value of similar magnitude to the "large" C_Q (129 kHz) determined for $(NH_4)_2WS_4$. We note that it is impossible to obtain a decent fit to the experimental spectrum in Figure 1c using a single set of C_Q and η_Q values. However, for a fit involving a Gaussian distribution of C_Q and η_Q values, an excellently fitted spectrum (Figure 1d) is obtained. The center values for the Gaussian distribution of the C_Q and η_Q parameters (Table 1) are in excellent agreement with the data for the "large" C_Q NH_4^+ ion in $(NH_4)_2WS_4$. The ^{14}N MAS NMR spectrum of Cs_2WS_4(D) in Figure 1e displays identical features to those observed for Cs_2WS_4(C) in Figure 1c (i.e., only the NH_4^+ site for $C_Q = 128 \pm 11$ kHz is observed), but with an intensity reduction of a factor of 5.4, determined from the total intensities for the spectra (Figure 1c and e).

Table 1. ^{14}N, ^{133}Cs, and ^{87}Rb Quadrupole Coupling (C_Q, η_Q) and Chemical Shift Parameters (δ_σ, η_σ, δ_{iso}) for A_2WS_4 (A = NH_4, Cs, Rb) from ^{14}N, ^{133}Cs, and ^{87}Rb MAS NMR Spectra[a]

compound/sites	C_Q (kHz)	η_Q	δ_σ(ppm)	η_σ	δ_{iso}[b] (ppm)
		$(NH_4)_2WS_4$[c]			
N(1)	129	0.18			−12.7
N(2)	48	0.12			−8.5
		Cs_2WS_4(C)[d]			
N(1)	128	0.00			−15.2
		Cs_2WS_4(D)[d,e]			
N(1)	128	0.00			−15.2
Cs(1)	307 (320)	0.01 (0.05)	−216	0.71	−214.0
Cs(2)	144 (100)	0.85 (0.81)	208	0.82	−134.0
		Rb_2WS_4(C)[f,g]			
N(1)	135	0.18			−13.0
N(2)	49	0.19			−9.3
Rb(1)	6970 (7940)	0.15 (0.28)	−125	0.00	−6.5
Rb(2)	1700 (1600)	0.90 (0.48)	109	0.17	13.5

[a] The values shown in parentheses for the ^{133}Cs and ^{87}Rb C_Q and η_Q parameters, below the experimental values, are those from the DFT (WIEN2k) calculations. The error limits for C_Q, η_Q, δ_σ, η_σ, and δ_{iso} vary according to the individual sample according to footnotes b−g. [b] The δ_{iso} values are relative to (^{14}N) solid NH_4Cl ± 0.3 ppm, (^{133}Cs) solid CsCl ± 0.3 ppm, and (^{87}Rb) 1.0 M aqueous $RbNO_3$ ± 0.5 ppm. [c] Error limits for $C_Q(^{14}N)$, ±3 kHz, and $\eta_Q(^{14}N)$, ± 0.03. [d] Standard deviation for $C_Q(^{14}N)$, ±11 kHz, and $\eta_Q(^{14}N)$, ± 0.06. [e] Error limits for $C_Q(^{133}Cs)$, ±10 kHz; $\eta_Q(^{133}Cs)$, ±0.05; $\delta_\sigma(^{133}Cs)$, ±10 ppm; and $\eta_\sigma(^{133}Cs)$, ± 0.10. [f] Standard deviation for $C_Q(^{14}N)$, ±13 kHz, and $\eta_Q(^{14}N)$, ±0.05. [g] Error limits for $C_Q(^{87}Rb)$, ±200 kHz; $\eta_Q(^{87}Rb)$, ±0.15; $\delta_\sigma(^{87}Rb)$, ±10 ppm; $\eta_\sigma(^{87}Rb)$, ±0.10.

To obtain further quantitative details on the degree of NH_4^+ substitution into only one of the two unique Cs^+ sites of the Cs_2WS_4 structure, several ^{133}Cs MAS NMR spectra have been recorded at a quantitative level for both samples C and D at various magnetic field strengths (14.1, 9.4, and 7.1 T). As an example, a 14.1 T (78.7 MHz) ^{133}Cs MAS NMR spectrum of Cs_2WS_4(D) is displayed in Figure 2a and clearly shows the resolution of two ssb manifolds for the two unique Cs^+ sites in Cs_2WS_4.[3] Spectral analysis (Table 1) combined with quantitative evaluations by integration of the ssb's for the two unique Cs^+ sites for all acquired ^{133}Cs MAS spectra give an average intensity ratio Cs(2)/Cs(1) = 1.189 ± 0.015 for Cs_2WS_4(C) and Cs(2)/Cs(1) = 1.040 ± 0.020 for Cs_2WS_4(D). The Cs-site numbering, 1 and 2, for

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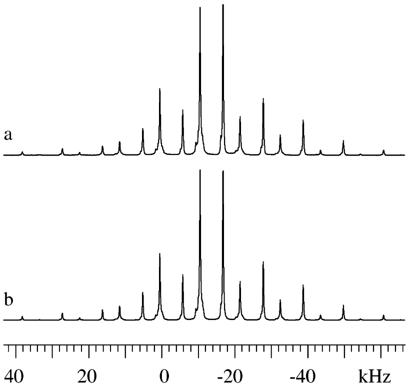

Figure 2. ^{133}Cs MAS NMR spectra of Cs_2WS_4(D) obtained at 78.67 MHz (14.1 T) and for $\upsilon_r = 6000$ Hz. (a) Experimental (928 scans, 24 h) and (b) simulated spectra showing the two nonequivalent Cs sites with a intensity ratio Cs(2)/Cs(1) = 1.040 (see text and Table 1).

Table 2. Composition and Distribution of NH_4^+ Ions Between the Two Cation Sites in Solid Solutions of $Cs_{2-z}(NH_4)_zWS_4$ and $Rb_{2-z}(NH_4)_zWS_4$ Prepared According to Two Different Methods

	concentrated solutions, method C: A_2WS_4(C)	dilute solutions, method D: A_2WS_4(D)
Cs(1)	$Cs_{0.841}(NH_4)_{0.159}(WS_4)_{0.5}$	$Cs_{0.962}(NH_4)_{0.038}(WS_4)_{0.5}$
Cs(2)	$Cs_{1.000}(NH_4)_{0.000}(WS_4)_{0.5}$	$Cs_{1.000}(NH_4)_{0.000}(WS_4)_{0.5}$
sum	$Cs_{1.841}(NH_4)_{0.159}WS_4$	$Cs_{1.962}(NH_4)_{0.038}WS_4$
anal.	$Cs_{1.829}(NH_4)_{0.171}WS_4$[a]	$Cs_{1.959}(NH_4)_{0.041}WS_4$[b]
Rb(1)	$Rb_{0.703}(NH_4)_{0.297}(WS_4)_{0.5}$	$Rb_{0.875}(NH_4)_{0.125}(WS_4)_{0.5}$
Rb(2)	$Rb_{0.780}(NH_4)_{0.220}(WS_4)_{0.5}$	$Rb_{0.901}(NH_4)_{0.099}(WS_4)_{0.5}$
sum	$Rb_{1.483}(NH_4)_{0.517}WS_4$	$Rb_{1.776}(NH_4)_{0.224}WS_4$
anal.	$Rb_{1.503}(NH_4)_{0.497}$ WS_4[c]	$Rb_{1.725}(NH_4)_{0.275}$ WS_4[d]

[a] The elemental nitrogen analysis (anal.) is 0.43 wt % N. [b] The elemental nitrogen analysis (anal.) is <0.1 wt % N. Calculated formula based on 0.1 wt % N. [c] The elemental nitrogen analysis (anal.) is 1.55 wt % N. [d] The elemental nitrogen analysis (anal.) is 0.83 wt % N.

the two cation sites of the A_2WS_4 samples in Table 1 refers to the A quadrupole nucleus having the largest and smallest C_Q value, respectively (vide supra). Considering the two formulas for the two unique cation sites with $C_Q(1)$ ("large") and $C_Q(2)$ ("small"), that is, $C_Q(1)$, $Cs_{1-x}(NH_4)_x(WS_4)_{0.5}$, and $C_Q(2)$, $Cs_{1-y}(NH_4)_y(WS_4)_{0.5}$, this gives two expressions which relate the experimental ^{14}N and ^{133}Cs MAS NMR relative intensities determined above for Cs_2WS_4(C) and Cs_2WS_4(D), ^{14}N MAS NMR, y/x, and ^{133}Cs MAS NMR, $(1 - y)/(1 - x)$.

From the above ^{133}Cs intensity ratios and $y = 0$ for both samples, very precise values are obtained for the site occupancies of the NH_4^+ ions (Table 2). Summations of the formulas for the two unique sites are compared in Table 2 for each of the two Cs_2WS_4 samples to the total composite formulas calculated based on the weight percent N results from the elemental nitrogen analyses. Excellent agreements between the results for the NMR-derived formulas and those based on the weight percent N from chemical analyses are observed. We also note that, from the ^{14}N NMR intensity ratio of 5.4:1 determined for Cs_2WS_4(C)/Cs_2WS_4(D), vide infra, a composite formula for Cs_2WS_4(D) has been calculated on the basis of the NMR summed formula for Cs_2WS_4(C) in Table 2, giving $Cs_{1.971}(NH_4)_{0.029}WS_4$, in agreement with the formulas presented in Table 2 for Cs_2WS_4(D).

A similar study is performed for the two rubidium samples Rb_2WS_4(C) and Rb_2WS_4(D) prepared by the same two methods, where the main difference between the Cs and Rb tetrathiotungstates is that the ^{14}N MAS NMR spectra for the Rb salts (Supporting Information) display ^{14}N resonances for *both* crystallographically unique NH_4^+ sites. Still, for both Rb samples, the integrated intensity for the N(1) site dominates over that for the N(2) site, that is, for Rb_2WS_4(C), $y/x = 0.74$, and for Rb_2WS_4(D), $y/x = 0.79$. Correspondingly, the ^{87}Rb MAS NMR spectra (Supporting Information) for the two samples show that the intensities determined from simulations/fitting (Table 1) of the experimental spectra are in accord with the ^{14}N MAS data, that is, for Rb_2WS_4(C), $(1 - y)/(1 - x) = 1.11$, and for Rb_2WS_4(D), $(1 - y)/(1 - x) = 1.03$. These simple equations result in the formulas for the two unique Rb sites of Rb_2WS_4(C) and Rb_2WS_4(D) shown in Table 2. An excellent agreement between the summed NMR formulas and those calculated on the basis of weight percent N is observed (Table 2).

These formulas show that a *lower* molar nitrogen content is always observed for Cs_2WS_4 compared to Rb_2WS_4, however, with a *higher* nitrogen content when more concentrated solutions are used in the synthesis. Since the ionic radii of NH_4^+ and Rb^+ are more similar than those of NH_4^+ and Cs^+, it is understandable from an energetic point of view that NH_4^+ has a preference for incorporation into Rb_2WS_4 versus into Cs_2WS_4.

Finally, DFT calculations (WIEN2k code[14]) of the ^{133}Cs and ^{87}Rb quadrupole coupling parameters (C_Q, η_Q) based on the crystal structures for Cs_2WS_4[3] and Rb_2WS_4[2] and following the same numbering of the two unique cations as in the reports of their crystal structures[2,3] give the values listed in parentheses next to the experimental data in Table 1. These calculated parameters are in good agreement with the experimental results and allow an unambiguous assignment of the cation site labeled 1 in the crystal structure to the site with the largest ^{14}N, ^{133}Cs, and ^{87}Rb C_Q values, that is, $C_Q(1)$ as used in Tables 1 and 2.

In conclusion, ^{14}N, ^{87}Rb, and ^{133}Cs MAS NMR provide detailed information on the preference of NH_4^+ for either of two different cation sites in $A_{2-z}(NH_4)_zWS_4$ (A = Cs, Rb) solid solutions. The preferences of NH_4^+ depend both on the type of site and on the host structure cation (Cs^+ or Rb^+). Thus, static ^{14}N NMR[15] could be useful in future metal−lipid binding studies.

Supporting Information Available: Synthesis, NMR spectroscopy, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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