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Synthesis of ^{17}O-Labeled Cs_2WO_4 and Its Ambient- and Low-Temperature Solid-State ^{17}O MAS NMR Spectra

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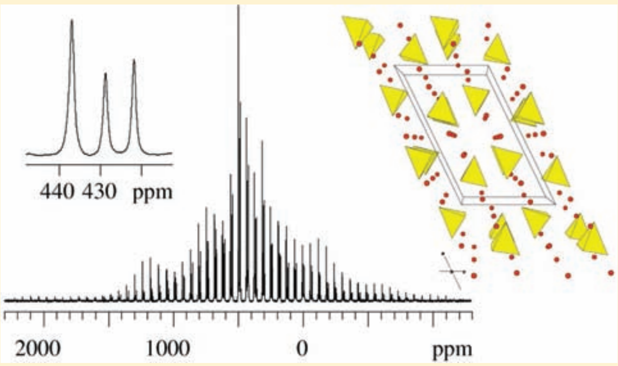
ABSTRACT: Following several seemingly straightforward but unsuccessful attempts to prepare a sample of ^{17}O-enriched Cs_2WO_4, we here report a simple, aqueous procedure for synthesis of pure Cs_2WO_4, if so desired, enriched in ^{17}O. The purpose for the preparation of ^{17}O-enriched Cs_2WO_4 is to record its solid-state ^{17}O MAS NMR spectrum, which would allow for a determination of its quadrupole coupling and chemical shift anisotropy (CSA) parameters and thereby for a comparison with the corresponding ^{33}S and ^{77}Se parameters in the related compounds M_2WS_4 and M_2WSe_4. These compounds are isomorphous and crystallize in the orthorhombic space group *Pnma*, and Cs_2WO_4 turns out to be the only alkali metal tungstate with the *Pnma* crystal structure. Therefore, it has been mandatory to use Cs_2WO_4 and not K_2WO_4 (space group $C2/m$) for which CSA data have previously been published, to achieve a reliable comparison with the ^{33}S and ^{77}Se data and thus allow assignment of the three different sets of ^{17}O NMR parameters to the three distinct oxygen sites (O(1,1), O(2), and O(3)) in the *Pnma* crystal structure of Cs_2WO_4. Because the ambient temperature ^{17}O MAS NMR spectrum of Cs_2WO_4 exhibits a dynamically broadened singlet, resorting to low-temperature (−83 °C) conditions at 21.15 T was necessary and resulted in a high-resolution ^{17}O MAS spectrum that allowed both ^{17}O quadrupole coupling and CSA parameters to be determined. As no quadrupole coupling data were obtained from the earlier investigation on K_2WO_4, the present results for Cs_2WO_4 prompted a reinvestigation of the ^{17}O MAS spectrum for K_2WO_4, which actually also shows the presence of ^{17}O quadrupole couplings for all three oxygen sites. These data for Cs_2WO_4 and K_2WO_4 are consistent and result in unambiguous assignments of the parameters to the three distinct oxygen sites in their crystal structures.



■ INTRODUCTION

Second only to hydrogen and carbon, the three light elements oxygen, nitrogen, and sulfur play an important role in organic, biological, and inorganic materials. While solid-state NMR detection of the spin-$^1/_2$ ^{15}N isotope is routinely performed in multidimensional (1D, 2D, and 3D) experiments, because of the availability of moderately inexpensive ^{15}N-labeled compounds, solid-state NMR detection of the three low-γ quadrupolar nuclei ^{14}N, ^{17}O, and ^{33}S can be much more difficult. Particularly, this is true for the low natural abundances of the ^{17}O (0.037%) and ^{33}S (0.76%) isotopes. The extremely high cost of ^{33}S-enriched compounds, compared to that of the relatively less expensive ^{17}O-enriched compounds, has been a tremendous challenge for the advancement of solid-state ^{33}S NMR. This is the most likely reason why less than 20 articles on solid-state ^{33}S NMR have so far appeared in the literature and why ^{17}O solid-state NMR articles are much more frequent. Our laboratory has recently made several contributions to the progress of ^{33}S MAS NMR.[1] Most of our ^{33}S MAS NMR studies have involved the tetrathiotungstate $(WS_4{}^{2-})$[1b−d] and tetrathiomolybdate $(MoS_4{}^{2-})$[1b,c] anions with $NH_4{}^+$ or $CH_3NH_3{}^+$ as counter cations but also published/unpublished results for some of their alkali metal cations on ^{14}N[2] and ^{33}S[3] MAS NMR. Single-crystal XRD studies[4] have shown that these materials are all isomorphous and crystallize in the orthorhombic space group *Pnma*, for example, the tetrathiotungstate series $(NH_4)_2WS_4$,[4a] $(CH_3NH_3)_2WS_4$,[4b] K_2WS_4,[4c] Rb_2WS_4,[4d] and Cs_2WS_4.[4e] Thus, the $WS_4{}^{2-}$ anions for each of these compounds are all crystallographically equivalent, whereas the four sulfur atoms of each $WS_4{}^{2-}$ ion constitute three unique sites: S(1,1), S(2), and S(3). In a recent solid-state ^{33}S MAS NMR investigation, we succeeded in simultaneously extracting precise ^{33}S quadrupole coupling and chemical shift anisotropy (CSA) parameters for the three nonequivalent sulfur atoms (S sites) in $(CH_3NH_3)_2WS_4$ from its highly complex natural abundance ^{33}S MAS NMR spectrum at 14.1 T.[1d] In addition to a simulation of this spectrum, we also proposed an assignment for the three sets of ^{33}S NMR parameters to the

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three crystallographically nonequivalent S sites[1d] within the *Pnma* crystal structures for both $(CH_3NH_3)_2WS_4$ (**1**)[4b] and $(NH_4)_2WS_4$ (**2**).[4a] These assignments were based on a comparison of the differences in local structure for the three S sites as obtained from their two crystal structures[4a,b] and relating these to the quite large differences observed for some of the ^{33}S quadrupole coupling (C_Q and η_Q) and CSA (δ_σ, η_σ, δ_{iso}) parameter values in **1** and **2**[1d] (also the electronic Supporting Information, ESI, in ref 1d). The resulting assignments of the spectral parameters to the S(1,1), S(2), and S(3) sites in **1** and **2** led to interesting consistencies and trends for the C_Q, η_Q parameters, as well as for the (δ_σ, η_σ, δ_{iso}) CSA data for **1** and **2**. Moreover, the trends observed for the isotropic and anisotropic ^{33}S chemical shift parameters for the three nonequivalent S atoms in the WS_4^{2-} anions of **1** and **2**, prompted us to assign the three corresponding (then unassigned) sets of ^{77}Se chemical shift parameters (ESI in ref 1d) recently reported for the three nonequivalent ^{77}Se (spin $I = {}^1/_2$) atoms in the WSe_4^{2-} ion of $(NH_4)_2WSe_4$,[5] which displays[6] *Pnma* structure as **1**[4b] and **2**.[4a]

These results prompted us to explore correlations between the ^{33}S quadrupole coupling (C_Q and η_Q) and CSA (δ_σ, η_σ, δ_{iso}) parameters cited above and the corresponding ^{17}O (spin $I = 5/2$) quadrupole coupling and CSA parameters determined for ^{17}O-enriched M_2WO_4 compounds. Powder XRD has shown that Cs_2WO_4 is orthorhombic and isomorphous with β-K_2SO_4 at room temperature,[7,8] by analogy with for example the crystal structures for $(CH_3NH_3)_2WS_4$ (**1**),[4b] $(NH_4)_2WS_4$ (**2**),[4a] and $(NH_4)_2WSe_4$,[6] which all crystallize in the orthorhombic space group *Pnma*. Moreover, in Cs_2WO_4 one of the two unique Cs^+ cations is surrounded by 9 oxygen atoms and the other by 10 oxygen atoms,[7] an arrangement identical to that found in the recently determined crystal structure for Cs_2WS_4 (space group *Pnma*), with one Cs^+ cation surrounded by 9 sulfur atoms and the other by 10 sulfur atoms.[4e] It turns out that Cs_2WO_4 is the only alkali metal tungstate, which belongs to space group *Pnma*.[7,8] Unfortunately, no solid-state ^{17}O NMR or other NMR data have been reported for Cs_2WO_4. However, it appears that a ^{17}O MAS NMR spectrum has been recorded and analyzed about 25 years ago for a 40 atom % ^{17}O-enriched sample of K_2WO_4,[9] which has a crystal structure $C2/m$[7] very much similar to the *Pnma* crystal structures for **1**, **2**, and $(NH_4)_2WSe_4$ as pointed out earlier.[1d] Although no ^{17}O quadrupole coupling (C_Q and η_Q), but only CSA (δ_σ, η_σ, δ_{iso}) parameters, were obtained from this ^{17}O MAS NMR spectrum for the three crystallographically nonequivalent oxygen sites in K_2WO_4,[9] we have proposed an assignment of these CSA data to the three nonequivalent ^{17}O sites based on a comparison with the corresponding CSA parameters for the M_2WE_4 (E = ^{33}S and ^{77}Se) structures[1d] (ESI in ref 1d).

In this study, we investigate the appearance of solid-state ^{17}O MAS NMR spectra of an about 10 atom % ^{17}O-enriched sample of Cs_2WO_4 at ambient (i.e., 293 K, 20 °C) and at about 190 K (−83 °C) for a comparison of the potentially determined ^{17}O quadrupole coupling (C_Q and η_Q) and CSA (δ_σ, η_σ, δ_{iso}) parameters with the corresponding ^{33}S parameters already determined for the two $[WS_4^{2-}]$ *Pnma* structures (**1** and **2**) cited above. Moreover, such a comparison should allow for an assignment of the solid-state ^{17}O NMR parameters to the three different O(1,1), O(2), and O(3) sites in Cs_2WO_4, which correspond to the similar sites in the *Pnma* structures for **1** and **2**. In addition, this comparison/assignment of the solid-state ^{17}O parameters for the *Pnma* structure of Cs_2WO_4 could also serve to confirm or possibly discard our proposed assignment for the three crystallographically nonequivalent O(1,1), O(2), and O(3) sites in K_2WO_4[1d] [ESI] based on the originally determined ^{17}O CSA (δ_σ, η_σ, δ_{iso}) parameters.[9] However, in our hands the incorporation of ^{17}O into Cs_2WO_4 does not appear to be just as simple as described for ^{17}O-enriched K_2WO_4 (i.e., ^{17}O-exchange into K_2WO_4 by heating a solution in $H_2{}^{17}O$ at 80 °C for 8 days)[9] mainly because of the readily formation of cesium polytungstates in aqueous solutions of Cs_2WO_4, in particular in warm[8] and acidic[10] solutions, as judged from several very complex solid-state ^{133}Cs MAS NMR spectra of samples isolated under these conditions. Thus, we here also describe a completely different approach for the synthesis of a pure sample of ^{17}O-enriched Cs_2WO_4, for which the purity has been checked based on the present first report of solid-state ^{133}Cs MAS NMR spectra and corresponding (C_Q and η_Q) and CSA (δ_σ, η_σ, δ_{iso}) parameters, determined for several of our samples of Cs_2WO_4.

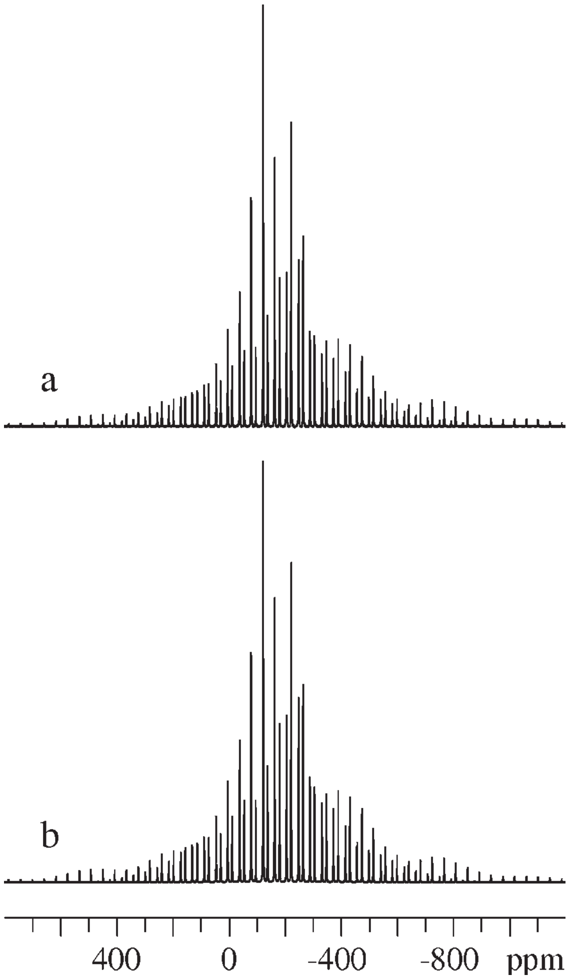

Figure 1. ^{133}Cs MAS NMR spectra of a sample of Cs_2WO_4, synthesized as described in the Experimental Section, obtained at 78.67 MHz (14.1 T) and for ν_r = 3300 Hz. (a) Experimental (48 scans in 72 min) and (b) simulated spectra showing the two nonequivalent Cs sites with a 1:1 intensity ratio.

Because it turns out that the solid-state ^{17}O MAS NMR investigation of our ^{17}O-enriched sample of Cs_2WO_4 has allowed determination of the ^{17}O quadrupole coupling (C_Q and η_Q) as well as the CSA (δ_σ, η_σ, δ_{iso}) parameters from an observation of both its central and satellite transitions (CT and STs respectively), we also report a reinvestigation of the about 25 year old ^{17}O MAS NMR spectrum of K_2WO_4[9] for which a set of only CSA (δ_σ, η_σ, δ_{iso}) parameters were obtained. Similar to the ^{17}O MAS NMR spectrum of Cs_2WO_4, our ^{17}O spectrum of K_2WO_4 shows resonances for both the CT and the four STs ($\pm^3/_2 \leftrightarrow \pm^1/_2$ and $\pm^5/_2 \leftrightarrow \pm^3/_2$), which have allowed a determination of both the ^{17}O quadrupole coupling (C_Q and η_Q) and CSA (δ_σ, η_σ, δ_{iso}) for K_2WO_4. The two sets of ^{17}O quadrupole coupling (C_Q and η_Q) parameters determined for Cs_2WO_4 and K_2WO_4 have allowed assignments of their solid-state NMR parameters to the three distinct oxygen sites, O(1,1), O(2), and O(3), consistent with the assignment for the ^{33}S parameters for **1** and **2**.

■ EXPERIMENTAL SECTION

Materials and Synthesis. Our first two samples of Cs_2WO_4 and K_2WO_4 were both purchased from Alfa Aesar. Whereas the sample of K_2WO_4 was very soluble in H_2O in accordance with the earlier report on its ^{17}O-exchange in a $H_2{}^{17}O$ solution at 80 °C for 8 days,[9] the sample of Cs_2WO_4 appeared almost insoluble in H_2O. This observation for the Alfa Aesar sample of Cs_2WO_4 clearly contradicts other reports on the H_2O solubility of Cs_2WO_4 (e.g., 0.86 g in 1 g H_2O at 17 °C[11] or the report on recrystallization of Cs_2WO_4 in H_2O at <10 °C[8]). In addition, the solid-state ^{133}Cs MAS NMR spectrum of the fresh Cs_2WO_4 sample from Alfa Aesar was a very complex, low-intensity spectrum, completely inconsistent with the two unique Cs sites of the *Pnma* structure of pure Cs_2WO_4 and also with our recently published ^{133}Cs MAS NMR spectrum for a sample of Cs_2WS_4[2], which has also been identified with the *Pnma* crystal structure.[4e]

A second sample of Cs_2WO_4 was obtained as a gift from the company 'Chemetall GmbH', D-60487 Frankfurt am Main, Germany, and simultaneously we undertook a new approach for the synthesis of Cs_2WO_4 using highly basic conditions in our laboratories (vide infra for a detailed description). These two Cs_2WO_4 samples (the German gift and our synthesized sample) were both identified as pure and identical samples according to the experimental and optimized fitted ^{133}Cs MAS NMR spectra as shown in Figure 1.

A ^{17}O-enriched sample of the Alfa Aesar K_2WO_4 material was easily synthesized according to the earlier reported, roughly 25 year old method (^{17}O-exchange in a 40% ^{17}O-enriched $H_2{}^{17}O$ solution at 80 °C for 8 days),[9] using 10% ^{17}O-enriched $H_2{}^{17}O$ purchased from CortecNet, France. Employing the exact same procedure for one of our two pure Cs_2WO_4 samples resulted in an unidentified, impure product according to both ^{17}O and ^{133}Cs MAS NMR spectroscopy. Thus, we here propose a new method for the synthesis of Cs_2WO_4 – one, which also allows for an easy ^{17}O-incorporation into the compound.

Synthesis of Cs_2WO_4 and Attempted Synthesis of ^{17}O-Labeled Cs_2WO_4. Twenty one grams (125 mmol) of $CsOH \cdot H_2O$ (Fluka) was dissolved in 2.5 mL H_2O (139 mmol) using a magnetic stirrer. This was followed by addition of 12.53 g of solid (yellow) $WO_3 \cdot H_2O$ (H_2WO_4, tungstic acid) (50 mmol, Aldrich), which was added in small portions at proper time intervals because of an extensive heating effect. Addition of all $WO_3 \cdot H_2O$ yielded a clear, colorless solution. Under vigorous stirring of this solution, 30 mL of methanol (CH_3OH) was added, which resulted in precipitation of a white powder. Centrifugation for 10 min at 1000 rpm separated the white powder from the clear supernatant liquid, which was removed. The white solid product was washed once in methanol, isolated by centrifugation as described above, and finally dried overnight under high vacuum. Yield: 13.43 g (52%). The product was identified as pure Cs_2WO_4 by powder XRD and solid-state ^{133}Cs MAS NMR spectroscopy (Figure 1).

Employing 2.5 mL of 10% $H_2{}^{17}O$ as opposed to the 2.5 mL ordinary H_2O for the synthesis described above in an attempt to obtain a ^{17}O MAS NMR spectrum, resulted in a similar yield; however, with an apparently very low incorporation of ^{17}O according to its ^{17}O MAS NMR spectrum. This is most likely due to a slow ^{17}O-exchange under the present synthetic conditions. Thus, in a second attempt to improve on the ^{17}O-exchange, the highly basic solution of Cs_2WO_4 (using 2.5 mL 10% $H_2{}^{17}O$) was kept at 80 °C in a Teflon-lined autoclave for 8 days before methanol was added to precipitate and isolate a hopefully higher ^{17}O-enriched Cs_2WO_4 sample. Indeed, this was confirmed by its ^{17}O MAS NMR spectrum, which indicated a somewhat higher but still quite low ^{17}O content compared to the quantity of 10% $H_2{}^{17}O$ used. Thus, an alternative improved route to the synthesis of ^{17}O-labeled Cs_2WO_4 was sought.

Improved Synthesis of ^{17}O-Labeled Cs_2WO_4. In a second attempt to improve on the degree of ^{17}O-incorporation into Cs_2WO_4, it was decided to alternatively ^{17}O-enrich one of the solid starting materials used in the new synthesis outlined above for Cs_2WO_4. Here, we describe an improvement for the synthesis of ^{17}O-enriched Cs_2WO_4 based on an initial ^{17}O-enrichment of the $WO_3 \cdot H_2O$ (tungstic acid) starting material using 10% $H_2{}^{17}O$, despite the fact tungstic acid is insoluable in cold H_2O and only slightly soluable in hot H_2O.

$WO_3 \cdot H_2O$ (3.14 g, 12.4 mmol) was added to 5 mL 10% $H_2{}^{17}O$ (~265 mmol) and the yellow slurry was transferred to a pyrex-glass ampule, which was then sealed off. The ampule was kept at 90 °C for 35 days and was shaken vigorously almost each day during this period. When the ampule was opened the settled solid residue of hopefully ^{17}O-enriched $WO_3 \cdot H_2O$ was isolated following removal of the supernatant H_2O layer, dried, and then showed a weight of 2.95 g corresponding to a yield of ~94%. Analysis of the resulting $WO_3 \cdot H_2O$ product by ^{17}O MAS NMR spectroscopy showed a quite intense set of ssbs, which at this stage was not subjected to a detailed spectral analysis but mainly served as an indicator for a decent ^{17}O-incorporation into the very insoluable $WO_3 \cdot H_2O$. Then, Cs_2WO_4 was prepared from 2.49 g of the ^{17}O-enriched $WO_3 \cdot H_2O$ (~10.0 mmol), which was added in small portions to a solution of 4.22 g of $CsOH \cdot H_2O$ (25.1 mmol) in 0.5 mL 10% $H_2{}^{17}O$ (26.3 mmol) following the same procedure as described above. The yield of ^{17}O-enriched Cs_2WO_4 was 1.85 g (3.6 mmol, 36%) and its identity confirmed by solid-state ^{133}Cs MAS NMR spectroscopy.

Solid-State MAS NMR Spectroscopy. ^{17}O and ^{133}Cs MAS NMR experiments on Cs_2WO_4 and K_2WO_4 at ambient temperature were performed at Aarhus University on a Varian Direct-Drive VNMRS-600 wide-bore spectrometer (14.1 T) at 81.34 and 78.67 MHz, respectively. High-field ^{17}O MAS NMR experiments were performed at the National High Magnetic Field Lab (NHMFL), Tallahassee. Ambient temperature ^{17}O MAS spectra of K_2WO_4 were also obtained on a Bruker 830-DRX narrow-bore spectrometer (19.6 T) at 112.99 MHz, whereas both ambient- and low-temperature ^{17}O MAS NMR experiments of Cs_2WO_4 used the Bruker 900 MHz (21.15 T) Avance spectrometer, equipped with a home-built wide-bore (105 mm) magnet, at a frequency of 122.09 MHz.

Varian Direct-Drive VNMRS-600 Spectrometer. The ^{17}O MAS NMR experiments on this spectrometer employed a Varian/Chemagnetics double resonance T3MAS probe for 7.5 mm zirconia rotors, whereas the ^{133}Cs MAS NMR experiments used a home-built 5 mm double resonance broadband MAS probe. The magic angle of $\theta = 54.736°$ was adjusted to the highest possible precision ($< \pm 0.005°$) for the ^{17}O MAS NMR experiments using ^{14}N MAS NMR on a sample of $NH_4H_2PO_4$, whereas for ^{133}Cs MAS NMR on the home-built 5 mm probe we used ^{23}Na MAS NMR and a sample of $NaNO_3$. The ^{17}O and ^{133}Cs experiments were spun at MAS frequencies of ν_r = 5000 and 3300 Hz respectively with a precision <1.0 Hz in ν_r, employing the experimental setup, combined with a Varian/Chemagnetics MAS speed controller, as recently described.[12] ^{17}O and ^{133}Cs rf field strengths were calibrated using a sample of 10% $H_2{}^{17}O$ and an aqueous solution of 1.0 M CsCl, respectively. The ^{17}O signal from 10% $H_2{}^{17}O$ and ^{133}Cs MAS resonance from solid CsCl, spinning at ν_r = 5000 Hz, were used as external references. 90° flip angles of $pw(90)_{liquid}$ = 6.5 and 6.0 μs were achieved

Table 1. ^{133}Cs Quadrupole Coupling (C_Q, η_Q) and Chemical Shift Parameters (δ_σ, η_σ, δ_{iso}) from ^{133}Cs MAS NMR Spectra of Cs_2WO_4[a] and Cs_2WS_4[b] Determined at 14.1 T[c]

sample	site	C_Q (kHz)	η_Q	δ_σ (ppm)	η_σ	δ_{iso} (ppm)	ψ, χ, ξ (degree)
Cs_2WO_4	Cs(1)	423	0.62	−88	0.40	−222.2	0, 13, 56
Cs_2WO_4	Cs(2)	213	1.00	128	0.26	−163.4	90, 16, 7
Cs_2WS_4	Cs(1)	307	0.01	−216	0.71	−214.0	
Cs_2WS_4	Cs(2)	144	0.85	208	0.82	−134.0	

[a] Data determined in this work for one of the Cs_2WO_4 samples (Figure 1) synthesized in this work. [b] The parameters reported for Cs_2WS_4 are those determined in ref 2. [c] The δ_{iso} values (relative to solid CsCl) have an error limit of ±0.3 ppm. The error limits for C_Q, η_Q, δ_σ, η_σ, and (ψ, χ and ξ) are ±10 kHz, ±0.05, ±10 ppm, ±0.10 and (±20, ±5, ±10), respectively.

for the ^{17}O and ^{133}Cs solutions for the two different probes, respectively. Thus, the actual value of 2.0 μs employed for both the solid-state ^{17}O and ^{133}Cs MAS experiments corresponds to liquid flip angles of 28° and 30°, respectively. Relaxation delays of 30 and 90 s were used for the ^{17}O and ^{133}Cs MAS experiments, respectively. For the ^{17}O MAS spectra, we acquired 2240 scans for the Cs_2WO_4 sample (i.e., a total experimental time of 19 h) and 2880 scans for the K_2WO_4 sample (i.e., a total experimental time of 24 h), whereas for the ^{133}Cs MAS spectra 48 scans were acquired (i.e., a total experimental time of 72 min).

Bruker DRX-830 Narrow-Bore 19.6 T Spectrometer. The high-field ^{17}O MAS NMR experiments for K_2WO_4 were performed at ambient temperature on this spectrometer (at 112.99 MHz), equipped with a Magnex narrow-bore (31 mm i.d.) magnet. A home-built (NHMFL) broadband 7 mm single-resonance MAS probe (29 mm o.d.), using 7 mm o.d. Bruker rotors (sample volume 225 μL) positioned at the magic angle of 54.74° were employed. The final ^{17}O MAS spectrum was acquired for a MAS ν_r = 5.0 kHz, liquid 18° flip-angle, 5 s relaxation delay, and 16 384 scans (i.e., a total experimental time of 23 h).

Bruker Avance-900 Wide-Bore 21.15 T Spectrometer. High-field, ambient-, and low-temperature ^{17}O MAS NMR spectra for the ^{17}O-enriched Cs_2WO_4 sample were acquired on the 21.15 T home-built wide-bore magnet (NHMFL) equipped with a 900 MHz Bruker Avance console. The experiments employed a home-built (NHMFL) wide-bore (89 mm o.d.) variable-temperature (VT) broadband 3.2 mm double-resonance MAS probe for which a 90° flip-angle $pw(90)_{liquid}$ = 6.4 μs was obtained for the ^{17}O resonance of ordinary H_2O. A value of pw = 1.2 μs, which corresponds to a liquid 17° flip-angle, was used for the MAS experiments, along with a 16 and 30 s relaxation delay for the acquisition of the ambient- (22 °C) and low-temperature (−83 °C) MAS spectra, respectively. The ^{17}O ambient-temperature MAS spectrum was acquired for ν_r = 15.04 kHz (i.e., the sample temperature is ~5−10 °C higher because of frictional heating) using 200 scans (i.e., a total experimental time of ~53 min), whereas the ^{17}O low-temperature MAS spectra were acquired for spinning frequencies of ν_r = 15.04 kHz (162 scans, total experimental time of 81 min) and ν_r = 4.825 kHz (1200 scans, total experimental time of 10 h).

Spectral Analysis. All ^{17}O and ^{133}Cs MAS NMR spectra have been analyzed using the *STARS* simulation software package. *STARS* (*SpecTrum Analysis for Rotating Solids*) was developed in our laboratory several years ago[13,14] and the original version of *STARS* was early on incorporated into Varian's *VNMR* software for SUN Microsystem computers and has been available from Varian Inc. as part of their *VNMR Solids* software package.[15] The present version of *STARS* used here has been upgraded during the past few years and is capable of simultaneously handling spectral parameters (i.e., quadrupole coupling (C_Q, η_Q), chemical shift (δ_{iso}, δ_σ, η_σ), and Euler angles (ψ, χ, ξ) relating the relative orientation for these two tensorial interactions) for up to eight different nuclear sites in the optimization of a fit to an experimental spectrum. In addition to these spectral parameters, the program can also include (*i*) deviation ($\Delta\theta$) from the magic-angle, (*ii*) rf bandwidth, (*iii*) rf offset, (*iv*) jitter in spinning frequency,[12] and (*v*) the linewidths (Lorentzian and/or Gaussian) in the iterative fitting procedure. This upgraded version of *STARS* has been incorporated into both the Varian *VnmrJ* software running on SUN Microsystems Ultra-5 workstations and the *VnmrJ* software running on a Linux RedHat PC.

The quadrupole coupling and CSA parameters are defined by

$$C_Q = eQV_{zz}/h \quad \eta_Q = (V_{yy} - V_{xx})/V_{zz} \tag{1}$$

$$\delta_\sigma = \delta_{iso} - \delta_{zz} \quad \eta_\sigma = (\delta_{xx} - \delta_{yy})/\delta_\sigma \tag{2}$$

$$\delta_{iso} = (1/3)(\delta_{xx} + \delta_{yy} + \delta_{zz}) = (1/3)\mathrm{Tr}(\delta) \tag{3}$$

using the convention

$$|\lambda_{zz} - (1/3)\mathrm{Tr}(\lambda)| \geq |\lambda_{xx} - (1/3)\mathrm{Tr}(\lambda)| \geq |\lambda_{yy} - (1/3)\mathrm{Tr}(\lambda)| \tag{4}$$

for the principal elements ($\lambda_{\alpha\alpha} = V_{\alpha\alpha}$, $\delta_{\alpha\alpha}$) of the two tensors. The relative orientation of the two tensors is described by the three Euler angles (ψ, χ, ξ), which correspond to positive rotations of the CSA principal axis system around z(ψ), the new y(χ), and the final z(ξ) axis.

RESULTS AND DISCUSSION

A typical experimental ^{133}Cs MAS NMR spectrum for a Cs_2WO_4 sample obtained by one of the improved synthetic procedures is shown in part a of Figure 1 for a spinning frequency ν_r = 3300 Hz. It shows two well-resolved patterns of spinning sidebands (ssbs), corresponding to the two unique Cs sites in the *Pnma* crystal structure of Cs_2WO_4,[7,8] in a clean spectrum without any impurity resonances. This spectrum, and thus ^{133}Cs MAS NMR, has served as a benchmark tool for characterizing the structure and purity of our standard and ^{17}O-enriched synthesized samples of Cs_2WO_4. We note that for several other spinning frequencies around ν_r = 3300 Hz (e.g., for ν_r = 5000 Hz), a severe overlap between the two sets of ssbs for the two Cs sites is observed, that is, an overlap that severely hinders the extraction of precise values for the quadrupole coupling and CSA parameters for the two Cs sites. The simulated spectrum, resulting from an optimized iterative fit of the anisotropic parameters to the experimental spectrum (part a of Figure 1), is shown in part b of Figure 1 and the corresponding final parameters are summarized in Table 1. For a comparison, Table 1 also lists our recently reported corresponding ^{133}Cs NMR parameters determined for the *Pnma* crystal structure of Cs_2WS_4.[2] Furthermore, DFT calculations of the electric field gradient (EFG) tensor for the two Cs-sites in Cs_2WS_4 has allowed assignment of the two sets of ^{133}Cs quadrupole coupling parameters (C_Q, η_Q) to these sites[2] in the crystal structure of Cs_2WS_4.[4e] The pair of ^{133}Cs spectral parameters in Table 1 for Cs_2WO_4 exhibit quite similar trends as the pair of Cs_2WS_4 parameters (e.g., in particular the approximate ratio of 2 between the two C_Q values ($C_Q(1)$ and $C_Q(2)$) for Cs_2WS_4 as well as for Cs_2WO_4), and we have therefore assigned the ^{133}Cs spectral parameters for the two Cs-sites in the *Pnma* crystal structure of Cs_2WO_4 to the same structural Cs-sites as was done for Cs_2WS_4.[2]

Following confirmation of the structure and purity for the synthesized ^{17}O-enriched Cs_2WO_4 sample, employing both ^{133}Cs MAS NMR and powder XRD, its 14.1 T ^{17}O MAS

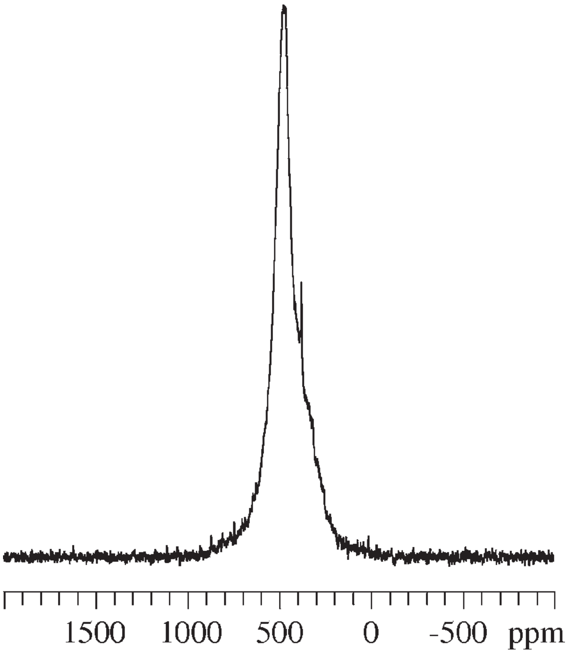

Figure 2. ^{17}O MAS NMR spectrum of ^{17}O-enriched Cs_2WO_4, synthesized based on 10 atom % $H_2{}^{17}O$ as described in the Experimental Section, obtained at 81.34 MHz (14.1 T), ν_r = 3300 Hz, 2240 scans in 19 h (overnight), and at ambient temperature. The narrow resonance at 377.9 ppm arises from the zirconia ceramic of the 7.5 mm rotor (text).

NMR spectrum (81.34 MHz) was recorded at ambient temperature for ν_r = 5000 Hz. Much to our surprise, the spectrum (Figure 2) appears as a quite broad singlet with fwhm ~8.7 kHz. This observation sharply contrasts the ambient-temperature ^{17}O MAS NMR spectrum, reported about 25 years ago,[9] of the structurally related ^{17}O-enriched K_2WO_4 salt, which shows distinct well-resolved CSA ssb patterns for the three nonequivalent O-sites (2:1:1) comprising the ^{17}O CT.[9] The tiny narrow resonance observed in the Cs_2WO_4 spectrum (Figure 2) on the right-hand side of the broad resonance at 377.9 ppm and several small, narrow resonances in the region around the broad resonance have been identified as the ^{17}O CT and the ssbs from the STs respectively arising from the natural abundance ^{17}O MAS spectrum of the zirconia ceramic for the 7.5 mm rotor. This was confirmed by recording the ^{17}O MAS spectrum of the empty zirconia rotor, which proved the origin of both the CT and the STs, observed earlier in several other ^{17}O MAS NMR studies.[16] The detection of the ^{17}O ssbs for the STs from the zirconia ceramic rotor material also shows that the precise setting of the magic angle (vide supra) has been preserved upon change of the probe tuning elements in going from ^{14}N to the ^{17}O MAS NMR experiments.

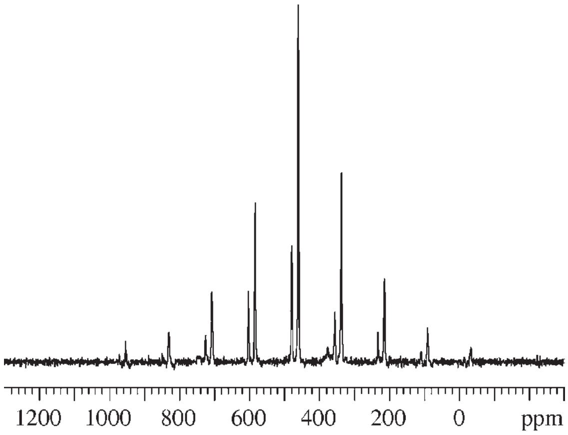

Figure 3. ^{17}O MAS NMR spectrum of the ^{17}O-enriched Cs_2WO_4 sample used in Figure 2 and obtained at 122.09 MHz (21.15 T), ν_r = 15.04 kHz, 162 scans in 1.5 h, and with a temperature of −83 °C (190 K). Two groups of resonances with an intensity ratio of 3:1 are observed (text).

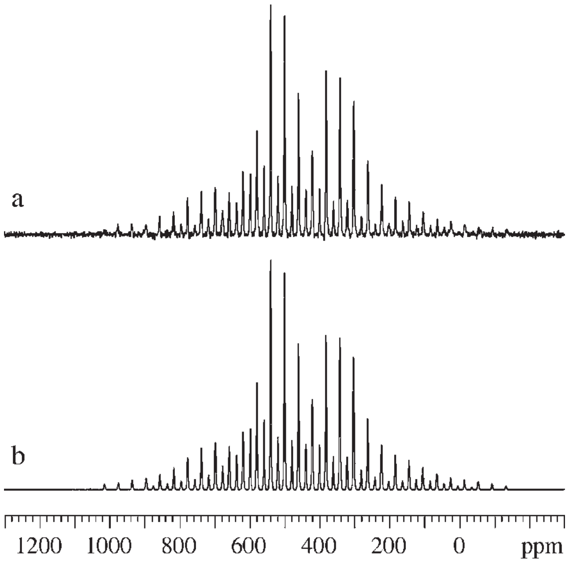

Figure 4. ^{17}O MAS NMR spectra of the ^{17}O-enriched Cs_2WO_4 sample used in Figure 2 and obtained at 122.09 MHz (21.15 T), ν_r = 4283 Hz, and for a temperature of −83 °C (190 K). (a) Experimental (1300 scans in 11 h) and (b) simulated spectra, where the simulated spectrum has been obtained as iterative fit to the experimental spectrum based on an intensity ratio of 2:1:1 for the O(1,1), O(2), O(3) sites (text).

Without sufficient low-temperature instrumentation available or the possibility for its use on the 14.1 T Varian VNMRS-600 and 19.6 T Bruker DRX-830 spectrometers, it was decided to go for recording of an ambient- and low-temperature (~ −80 °C) ^{17}O MAS NMR spectra of the ^{17}O-enriched Cs_2WO_4 sample on the 21.15 T Bruker Avance-900 ultra wide-bore spectrometer. The purpose was to check if the apparent scrambling, observed in the ^{17}O MAS NMR spectrum at 14.1 T for the expected three nonequivalent ^{17}O sites, could be stopped on the NMR time scale, thereby resulting in a spectrum with well-resolved resonances under these conditions. The 21.15 T (122.09 MHz) ^{17}O MAS NMR of Cs_2WO_4 at ambient temperature (not shown) exhibits the exactly same features as the 14.1 T spectrum in Figure 2, including a fwhm = 8.8 kHz. However, by lowering the temperature of the sample to −83 °C, the ^{17}O MAS NMR spectrum for ν_r = 15.04 kHz splits into two sets of widely spaced ssb patterns with an intensity ratio of 3:1 and a separation of 18.6 ppm (2271 Hz at 122.09 MHz) as shown in Figure 3. Because the *Pnma* crystal structure determined for Cs_2WO_4[4e] would predict the observation of three different O sites, O(1,1), O(2), and O(3), with an intensity ratio 2:1:1, this shows that the spectrum for one of the two low-intensity O sites (O(2) or O(3)) accidentally coincides with that for the O(1,1) site. This contrasts not only the ^{17}O MAS NMR spectrum of K_2WO_4,[9] which has a

Table 2. ^{17}O Quadrupole Coupling (C_Q, η_Q) and Chemical Shift Parameters (δ_σ, η_σ, δ_{iso}) for Cs_2WO_4 Determined from ^{17}O MAS NMR Spectra of ^{17}O-Enriched Cs_2WO_4 Recorded at 21.15 T and −83 °C[a]

site	C_Q (kHz)	η_Q	δ_σ (ppm)	η_σ	δ_{iso} (ppm)	ψ, χ, ξ (degree)
O(1,1)	278	0.42	179	0.48	459.5	0, 77, 0
O(2)	216	0.97	211	0.03	459.8	0, 89, 90
O(3)	241	0.58	256	0.08	478.2	90, 92, 0
O(1,1,1)[b]	276	0.25	204	0.00	459.6	163,90, 87
O(3)	241	0.58	256	0.08	478.2	90, 92, 0

[a] The δ_{iso} values (relative to aqueous $H_2{}^{17}O$) have an error limit of ±0.5 ppm. The error limits for C_Q, η_Q, δ_σ, η_σ and (ψ, χ and ξ) are ±10 kHz, ±0.05, ±10 ppm, ±0.10 and (±20, ±5, ±10), respectively. [b] Results from an analysis of the experimental spectrum in part a of Figure 4 assuming only two different O sites with an intensity ratio of 3:1, O(1,1,1):O(3) (text).

crystal structure $C2/m$[7] very much related to *Pnma* but also the three S-sites, S(1,1), S(2), and S(3), observed in the ^{33}S MAS NMR spectra for the two isostructural (*Pnma*) tetrathiotungstates $(NH_4)_2WS_4$[1b,c] and $(CH_3NH_3)_2WS_4$.[1d]

To retrieve the ^{17}O anisotropic interaction parameters for the three different oxygen sites with as high a precision as possible at this temperature, a ^{17}O MAS NMR spectrum was recorded for the lower spinning speed of ν_r = 4283 Hz and at −83 °C. This should allow for an increased number of ssbs for the two ssb patterns to enter the iterative parameter-fitting process. This experimental ^{17}O MAS NMR spectrum is shown in part a of Figure 4 along with its final optimized/simulated spectrum in part b of Figure 4. The spectrum in part b of Figure 4 results from an optimized fit to the experimental spectrum for which all three sets of spectral parameters (i.e., the quadrupole coupling (C_Q, η_Q), chemical shift (δ_{iso}, δ_σ, η_σ), and Euler angles (ψ, χ, ξ)) for the O(1,1), O(2), and O(3) sites were allowed to vary independently, combined with a determination of the error limits for these parameters and for the precisions in the setting of the experimental parameters (e.g., $\Delta\nu_r$ and $\Delta\theta$) using our *STARS* software.[13,14] The corresponding final sets of optimized parameters are summarized in Table 2. It could be argued that the experimental ^{17}O MAS NMR spectrum in part a of Figure 4 may also be analyzed assuming only two different O-sites with an intensity ratio of 3:1 (O(1,1,1):O(3)), corresponding to rotation about one of the W−O bonds for the tetrahedral $WO_4{}^{2-}$ anion being the first step in the process of stopping the complete scrambling of all four oxygen atoms, as observed from the ambient ^{17}O MAS NMR spectrum in Figure 2. Clearly, such an analysis would not be consistent with the *Pnma* crystal structure for Cs_2WO_4. Anyway, we performed the analysis, including an optimized fit (not shown) to the spectrum in part a of Figure 4, and the results are shown in Table 2. We note that the rms error from this fit is somewhat larger than that obtained above using the *Pnma* space group model and also that the simulated spectrum from the *Pnma* model shows a slightly better resemblance with the experimental spectrum. Thus, in the following we use the data from the *Pnma* model for comparisons with corresponding ^{17}O, ^{33}S, and ^{77}Se data in structurally related materials.

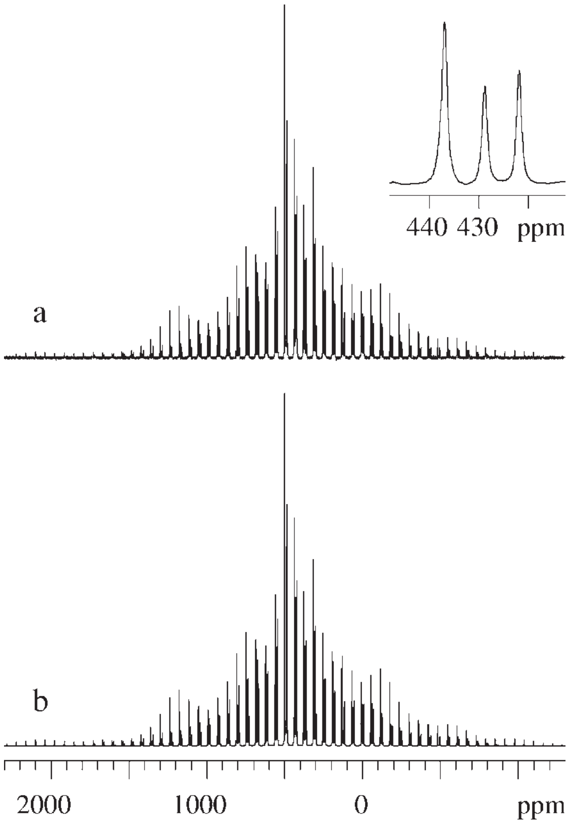

Figure 5. ^{17}O MAS NMR spectra of ^{17}O-enriched K_2WO_4, prepared by exchange with 10 atom % $H_2{}^{17}O$ as described in the Experimental Section and according to an earlier recipe,[9] obtained at 81.34 MHz (14.1 T), ν_r = 5000 Hz, and at ambient temperature. (a) Experimental (2880 scans in 24 h), where the insert shows an expansion of the three isotropic resonances, and (b) simulated spectrum using the optimized parameters listed in Table 3 for the 14.1 T parameters.

In comparison to the exploratory ^{17}O MAS NMR study on K_2WO_4 by Schramm and Oldfield[9] (vide infra), the most striking result seen from the ^{17}O data in Table 2 is the requirement to include the ^{17}O quadrupole coupling (C_Q and η_Q) as well as the CSA (δ_σ, η_σ, δ_{iso}) interaction parameters for all three oxygen sites in the fitting procedure, to arrive at a decent fit for the ^{17}O MAS spectrum of Cs_2WO_4. This follows from the original 11.7 T ^{17}O MAS spectrum for the CT in K_2WO_4[9] at ambient temperature, which exhibits 10 groups of three lines for ν_r = 3.2 kHz with no indication of measurable quadrupole interactions for the three O(1,1), O(2), and O(3) sites and therefore was analyzed considering the CSA interaction only.[9] Thus, with the present ^{17}O results obtained for Cs_2WO_4, we decided to perform a reinvestigation of the ambient temperature ^{17}O MAS NMR spectrum for K_2WO_4, using a synthesized ~10% ^{17}O-enriched sample (Experimental Section), to look for possible signs of ^{17}O quadrupole interactions by taking advantage of the STs.

The complete experimental ^{17}O MAS NMR spectrum (i.e., including both the CTs and all STs) for K_2WO_4 at 14.1 T and ν_r = 5000 Hz is shown in part a of Figure 5 and is fully consistent with the crystal structure exhibiting three crystallographically nonequivalent oxygen sites (O(1,1), O(2), O(3)).[7] Most importantly, the appearance of this spectrum differs significantly from the originally published ^{17}O MAS NMR spectrum[9] in that the STs give rise to numerous ssbs outside the region of the CTs for all three sites. In addition, within the spectral region for the CTs the ssbs for the STs make substantial contributions to the intensities of the ssbs for the CTs. Therefore, spectral analysis was performed for the complete manifolds of ssbs for all CTs and

Table 3. ^{17}O Quadrupole Coupling (C_Q, η_Q) and Chemical Shift Parameters (δ_σ, η_σ, δ_{iso}) for K_2WO_4 from ^{17}O MAS NMR Spectra of ^{17}O-Enriched K_2WO_4 at 14.1 and 19.6 T[a]

exp	sites	C_Q (kHz)	η_Q	δ_σ (ppm)	η_σ	δ_{iso} (ppm)	ψ, χ, ξ (degree)
14.1 T	O(1,1)	486	0.12	212	0.34	437.0	40, 89, 0
19.6 T	O(1,1)	482	0.15	215	0.22	436.9	40, 84, 0
11.7 T[b]	O(1,1)			220	0.15	437	–
14.1 T	O(2)	320	0.81	215	0.16	421.6	30, 35, 0
19.6 T	O(2)	326	0.80	214	0.15	421.5	50, 36, 0
11.7 T[b]	O(2)			214	0.30	422	–
14.1 T	O(3)	366	0.51	211	0.02	428.6	60, 63, 0
19.6 T	O(3)	367	0.51	224	0.18	428.5	90, 62, 0
11.7 T[b]	O(3)			227	0.22	429	–

[a] The δ_{iso} values (relative to $H_2{}^{17}O$) have an error limit of ±0.5 ppm. The error limits for C_Q, η_Q, δ_σ, η_σ and (ψ, χ, and ξ) are ±5 kHz, ±0.05, ±8 ppm, ±0.10 and (±20, ±5, and ξ = ±10 for O(2) and O(3) and ξ = ±15 for O(1,1)), respectively. It is noted that the atomic numbering used here for the three different O sites, O(1,1), O(2), O(3), is identical to that used in a recent study[1d] and that it differs from that used in the report of the crystal structure for K_2WO_4[7]. [b] The principal axis values from ref 9 are converted to the δ_σ, η_σ, δ_{iso} convention used here (Experimental Section).

STs in terms of ^{17}O chemical shifts (δ_σ, η_σ, δ_{iso}) and quadrupole coupling (C_Q, η_Q) parameters along with the three Euler angles (ψ, χ, ξ) for the three O(1,1), O(2), O(3) sites with relative intensities of 2:1:1. After a few preliminary spectral simulations, a final combined and simultaneous three-site optimized iterative fit to the manifolds of ssbs for the experimental spectrum results in the ^{17}O spectral parameters summarized in Table 3 for the three independent oxygen sites in K_2WO_4. The simulated spectrum (part b of Figure 5) corresponding to these parameters shows an excellent agreement with the experimental spectrum.

To enhance the effects of the ^{17}O CSAs relative to the first-order quadrupole interactions, a ^{17}O MAS NMR spectrum has been recorded at the higher field of 19.6 T for ν_r = 5000 Hz with the purpose of changing the relative intensities within the three manifolds of ssbs and thereby the appearance of the full ^{17}O MAS NMR spectrum. This high-field ^{17}O MAS spectrum would allow for an independent second spectral analysis, including determination of the anisotropic parameters for comparison with the data obtained at 14.1 T, and thereby serve as an independent check on the precision of the spectral parameters at 14.1 T. The experimental 19.6 T ^{17}O MAS NMR spectrum in part a of Figure 6 and its corresponding optimized simulated spectrum in part b of Figure 6 are in mutual accordance, similar to the two corresponding 14.1 T spectra in Figure 5. The spectral parameters determined from the 19.6 T spectrum are summarized in Table 3 for an easy comparison with the data obtained at 14.1 T and the ^{17}O CSA parameters originally determined at 11.7 T.[9] This comparison of the ^{17}O quadrupole coupling (C_Q, η_Q) and CSA (δ_σ, η_σ, δ_{iso}) parameters determined at 14.1 and 19.6 T for K_2WO_4 shows that the two sets of data are in excellent agreement and both sets are within the experimental errors listed for the parameters in the footnotes of Table 3. Moreover, it is noteworthy that the early reported CSA parameters determined at 11.7 T[9] (Table 3) are also in very good agreement with the 14.1 and 19.6 T data obtained here. However, it is quite remarkable that the early ^{17}O CSA parameters determined from the ^{17}O MAS spectrum at 11.7 T[9] exhibit a very good agreement with the data of the present study. The reason is that simulated ^{17}O MAS spectra performed in this study for the CTs and STs at 11.7 T (67.76 MHz) and ν_r = 3.2 kHz (i.e., the experimental setup used in ref 9), using the (C_Q, η_Q) and the (δ_σ, η_σ, δ_{iso}) data determined here, show that the STs make significant intensity contributions to the total (ST + CT) intensities for the 10 group of CT resonances observed in ref 9 for the individual O(1,1), O(2), O(3) sites. In particular, this holds for the O(2) and O(3) sites (i.e., those having the lowest C_Q values) for which the STs for the 6 CT resonances of lowest intensity contribute between 50 and 90% to the total CT intensities. Indeed, a simulation using the CSA (δ_σ, η_σ, δ_{iso}) parameters only (i.e., C_Q = 0) shows a spectrum almost identical to the spectrum published by Schramm and Oldfield[9] and therefore indicates that the STs are lost in their spectrum. Although one could speculate on several reasons, which could cause this observation, our simulations show that neither (*i*) the magic-angle setting, which has been very well adjusted because $\Delta\theta \sim 0°$ according to the simulations, nor (*ii*) jitter in spinning frequency can account for the loss of the STs. Thus, we can only speculate that a strange, unfortunate combination of other experimental conditions (e.g., excitation (~90°),[9] relaxation delay, different relaxation times for the CTs and STs, detection) may have caused the loss of the STs in the detection of the earlier published spectrum.[9]

Most importantly, the determination of the ^{17}O quadrupole coupling (C_Q, η_Q) parameters for both Cs_2WO_4 and K_2WO_4 in

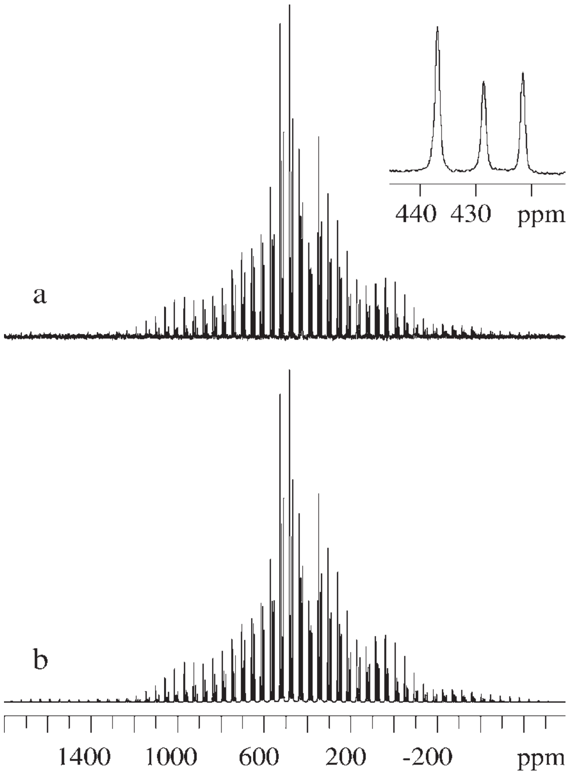

Figure 6. ^{17}O MAS NMR spectra of ^{17}O-enriched K_2WO_4, using the sample from Figure 5, obtained at 112.99 MHz (19.6 T) acquired using a 7.0 mm Bruker rotor (sample volume 225 μL), ν_r = 5000 Hz, and at ambient temperature. (a) Experimental (16 384 scans in 23 h), where the insert shows an expansion of the three isotropic resonances, and (b) simulated spectrum using the optimized parameters listed in Table 3 for the 19.6 T parameters.

Table 4. **^{17}O Quadrupole Coupling (C_Q, η_Q) and Chemical Shift Parameters (δ_σ, η_σ, δ_{iso}) for Cs_2WO_4 (−83 °C) and K_2WO_4 Determined from ^{17}O MAS NMR Spectra of ^{17}O-Enriched Cs_2WO_4 and K_2WO_4 and Compared with Corresponding Earlier Reported and Assigned[1d] ^{33}S and ^{77}Se Parameters for $(CH_3NH_3)_2WS_4$ (1),[1d] $(NH_4)_2WS_4$ (2),[1d] and $(NH_4)_2WSe_4$;[5] the Assignments of the ^{17}O Parameters to the Individual Oxygen Sites in Their Crystal Structures Follow from This Comparison (Text)[a]**

sample/sites	C_Q (kHz)	η_Q	δ_σ (ppm)	η_σ	δ_{iso} (ppm)	ψ, χ, ξ (degree)	ref
Cs_2WO_4							
O(1,1)	278	0.42	179	0.48	459.5	0, 77, 0	
O(2)	216	0.97	211	0.03	459.8	0, 89, 90	
O(3)	241	0.58	256	0.08	478.2	90, 92, 0	
K_2WO_4[b]							
O(1,1)	482	0.15	215	0.22	436.9	40, 84, 0	
O(2)	326	0.80	214	0.15	421.5	50, 36, 0	
O(3)	367	0.51	224	0.18	428.5	90, 62, 0	
K_2WO_4							
O(1,1)			220	0.15	437		9
O(2)			214	0.30	422		9
O(3)			227	0.22	429		9
$(CH_3NH_3)_2WS_4$							
S(1,1)	794	0.87	401	0.11	545.3	5, 85, 21	1d
S(2)	847	1.00	344	0.10	473.1	76, 78, 26	1d
S(3)	965	0.40	383	0.25	491.5	94, 89, 1	1d
$(NH_4)_2WS_4$							
S(1,1)	708	0.77	389	0.16	542.3	147, 10, 2	1d
S(2)	531	0.08	380	0.05	495.8	53, 4, 16	1d
S(3)	620	0.14	396	0.35	518.7	87, 47, 73	1d
$(NH_4)_2WSe_4$[c]							
Se(1,1)			926	0.03	1338		5
Se(2)			864	0.01	1155		5
Se(3)			892	0.32	1256		5

[a] The error limits for the ^{33}S parameters C_Q, η_Q, δ_σ, η_σ, and δ_{iso} are identical to those published,[1d] i.e., ±0.07 kHz, ±0.05, ±4 ppm, ±0.05, and ±0.5 ppm, respectively. The δ_{iso} values are relative to neat CS_2 (the ^{33}S chemical shift of 1.0 M Cs_2SO_4 is 333 ppm relative to CS_2) and include corrections for the second-order quadrupolar shifts. The ψ, χ, and ξ Euler angles for the ^{33}S parameters are those directly obtained from the optimized fitting to the individual S sites with the smallest error limits observed for the χ angle of ±6°.[1d] For the error limits of the ^{17}O parameters for Cs_2WO_4 and K_2WO_4 we refer to the footnotes for these parameters in Tables 3 and 4, respectively. [b] The ^{17}O parameters shown here for K_2WO_4 are those determined from the 19.6 T spectrum and presented in Table 3 because of the increased sensitivity for the ^{17}O CSA parameters to the highest applied magnet field strengths. [c] The principal axis values from ref 5 are converted to the δ_σ, η_σ, δ_{iso} convention used here (Experimental Section).

the present study will allow for a definite assignment of the ^{17}O spectral parameters to the different O(1,1), O(2), O(3) sites in the crystal structure for the WO_4^{2-} anion of these samples by an additional comparison with the ^{33}S quadrupole coupling parameters for the equivalent S(1,1), S(2), S(3) sites[1d] in the crystal structure for the WS_4^{2-} anions in $(CH_3NH_3)_2WS_4$ (**1**)[4b] and $(NH_4)_2WS_4$ (**2**)[4a] (vide supra). As mentioned in the introduction, we recently proposed an assignment of the published[9] three sets of CSA (δ_σ, η_σ, δ_{iso}) parameters for K_2WO_4 to the three nonequivalent ^{17}O sites in its crystal structure based on a comparison with the corresponding ^{33}S and ^{77}Se CSA parameters for some M_2WE_4 (E = ^{33}S and ^{77}Se) structures[1d] (ESI in ref 1d). To take full advantage of the complete ^{17}O spectral parameters obtained here for Cs_2WO_4 and K_2WO_4 in a comparison with the earlier reported ^{33}S and ^{77}Se data for **1**, **2** and $(NH_4)_2WSe_4$ respectively we have summarized the spectral parameters for all the compounds in Table 4 and with the assignments according to their crystal structures, which will now be briefly discussed.

First, we note that the atomic numbering used here for the three different O sites, O(1,1), O(2), O(3), with a 2:1:1 intensity ratio, is identical to that in our recent study[1d] for the assignment of NMR parameters to the S, Se, and O sites in **1**, **2**, $(NH_4)_2WSe_4$, and K_2WO_4. This numbering differs from that used in the report of the crystal structure for K_2WO_4[7] (space group *C*2/*m* very similar to *Pnma*) and in the original report for the $(NH_4)_2WS_4$ (**2**) structure[4a] (space group *Pnma*), which accordingly have been changed to that employed here. The assignment of the resulting spectral parameters for the two equivalent chalcogens to the E(1,1) sites (E = O, S, Se) for the samples in Table 4 is straightforward based on the relative intensities of 2:1:1 used in the spectral analysis for the three group of resonances. However, a distinction between and thus assignment of the parameters to the E(2) and E(3) sites (E = O and Se) may not be trivial; however, for the present samples it immediately follows from a comparison with the spectral parameters determined in our exploratory work on the assignment for S(2) and S(3) in $(CH_3NH_3)_2WS_4$ (**1**) and $(NH_4)_2WS_4$ (**2**).[1d] Thus, for the assignments shown in Table 4 we observe excellent consistencies between almost all of the spectral parameters not only for the E(2) and E(3) sites but also for the E(1,1) sites. For the ^{17}O and ^{33}S quadrupole coupling parameters, we note that the C_Q values for the E(3) sites are always larger than for the E(2) sites, while η_Q for the E(2) sites approaches values $\eta_Q \sim 1$ except for $(NH_4)_2WS_4$ (heavily hydrogen bonded structure). Similarly, for the ^{17}O, ^{33}S, and ^{77}Se chemical shift parameters (δ_σ, η_σ, δ_{iso}) we observe that the δ_σ values for the E(3) sites are in all cases larger than for the E(2) sites, whereas η_σ for the E(2) sites is close to a value $\eta_\sigma \sim 1$. Furthermore, for the isotropic chemical shifts (δ_{iso}) we note that δ_{iso} for the E(3) sites is larger compared to the E(2) sites for all samples, while δ_{iso} for the E(1,1) sites has the largest value of the three, that is, E(1,1) > E(3) > E(2) in all cases, except for the −83 °C ^{17}O MAS spectrum of Cs_2WO_4. Finally, it is noted that the tentative assignment we proposed recently[1d] (ESI in ref 1d) for the old ^{17}O CSA parameters[9] determined for K_2WO_4, and which was mainly based on the order for the three isotropic chemical shifts, has now been fully confirmed following the determination of the ^{17}O quadrupole coupling parameters for both Cs_2WO_4 and K_2WO_4 in this work.

CONCLUSIONS

Following the successful synthesis of a ^{17}O-enriched sample of Cs_2WO_4 and also for an earlier described sample of K_2WO_4, we have succeeded in determining ^{17}O quadrupole coupling parameters along with the ^{17}O CSA data for these two samples. The ^{17}O quadrupole coupling data have allowed unambiguous assignments for the three different sets of spectral parameters for each sample to the three nonequivalent oxygen sites, O(1,1), O(2), O(3), in the crystal structures for Cs_2WO_4 (space group *Pnma*) and K_2WO_4 (space group C2/*m*). Full consistencies are observed for the ^{17}O spectral parameters with those for some other chalcogen spin nuclei (^{33}S and ^{77}Se) in related and isostructural materials.

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