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New Opportunities in Acquisition and Analysis of Natural Abundance Complex Solid-State ^{33}S MAS NMR Spectra: $(CH_3NH_3)_2WS_4$

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Electronic Supplementary Information
Contents

Differences in Crystal Structures for $(CH_3NH_3)_2WS_4$ and $(NH_4)_2WS_4$ from X-Ray Diffraction

The environments of S atoms as determined from X-ray diffraction studies of the crystal structure for the two compounds $(CH_3NH_3)_2WS_4$[1] and $(NH_4)_2WS_4$[2] are illustrated below. Note that the numbering scheme has been chosen on the basis of the crystal structure of $(CH_3NH_3)_2WS_4$ [1].

Some further information:

$(CH_3NH_3)_2WS_4$, space group *Pnma*

Bond distances (Å): W-S1: 2.1862(13), W-S2: 2.199(2), W-S3: 2.2010(18)

Bond angles: S1-W-S1: 108.46(7), S1-W-S2: 108.62(5), S1-W-S3: 110.45(5), S2-W-S3: 110.18(8)

Eight S···H contacts (neglecting two C-H···S) with N-S separations between 3.227(7) and 3.562(1) Å, and corresponding N-H···S angles ranging from 121 to 152°.

$(NH_4)_2WS_4$, space group *Pnma*

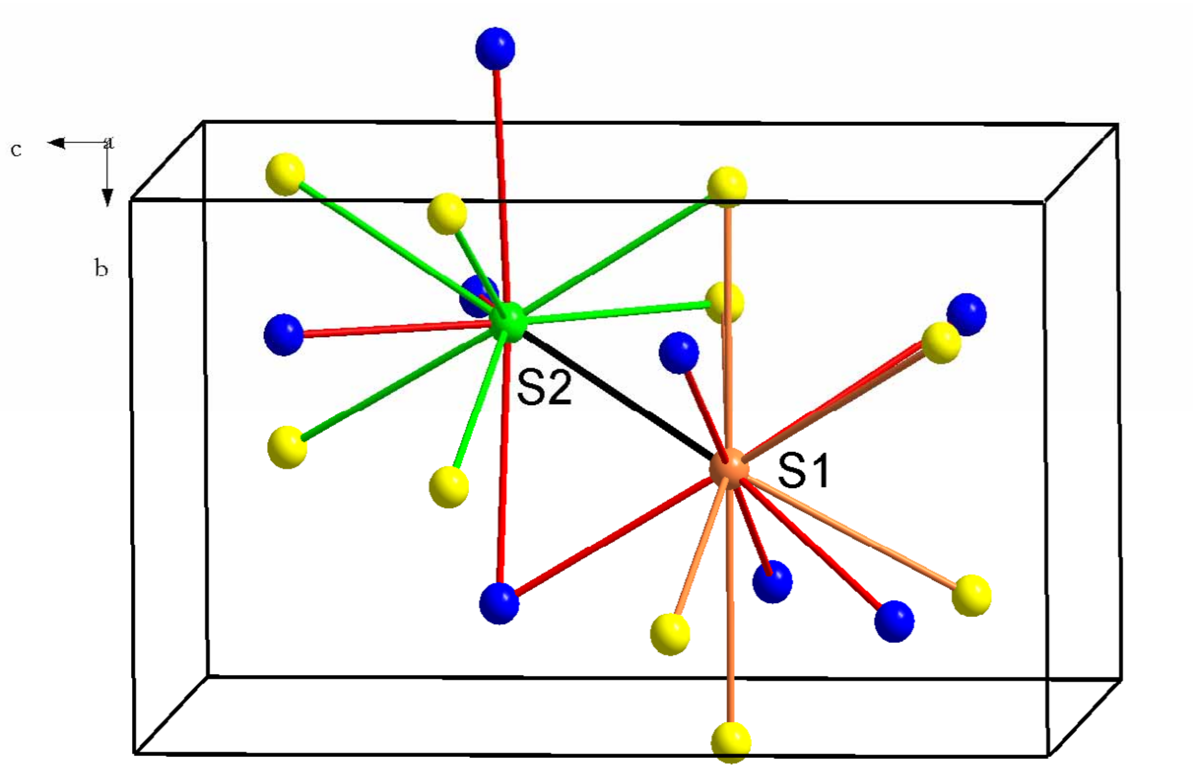
Bond distances (Å): W-S1: 2.1870(7), W-S2: 2.1856(11), W-S3: 2.2090(10)

Bond angles: S2-W-S1 109.25(3), S1-W-S1 108.23(4), S2-W-S3 110.33(4), S1-W-S3 109.87(2)

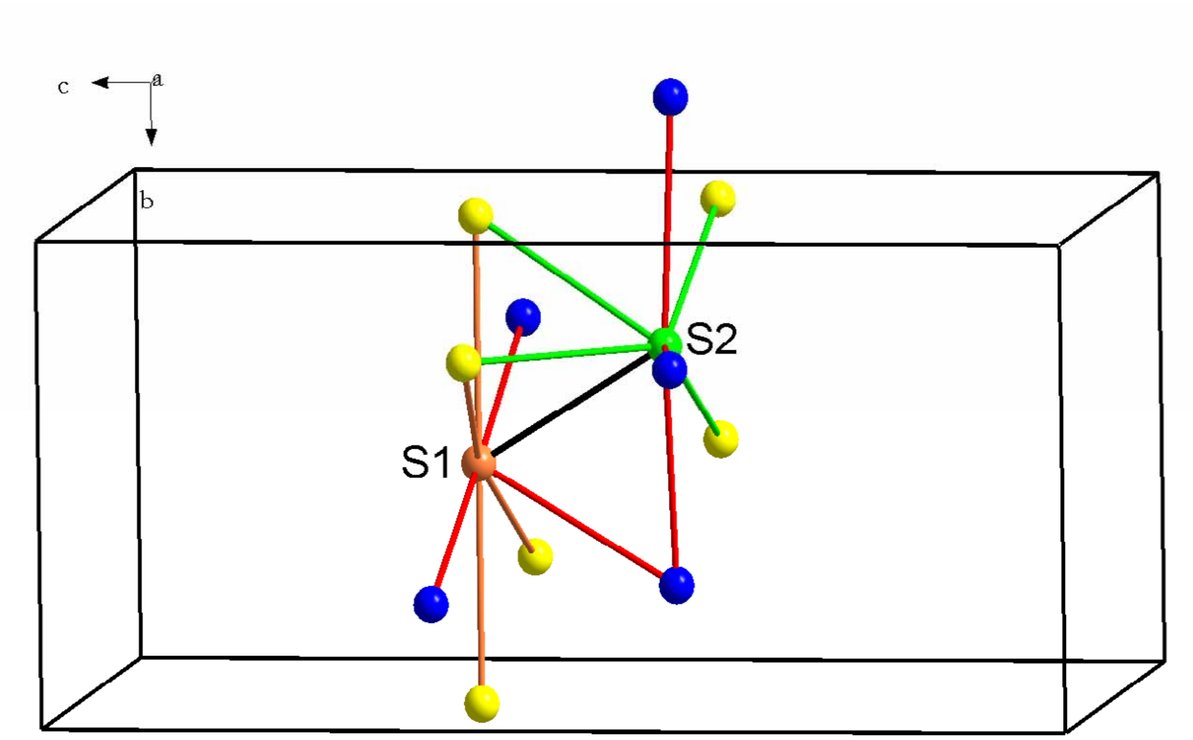
Thirteen S···H contacts with N-S separations between 3.242(4) and 3.633(4) Å, corresponding angles: 118 – 149°.

In the following figures the environments of the different S atoms are shown. S-W bonds are neglected. Note that in all drawings the lines between the atoms do not indicate direct bonding interactions. They are drawn for a better visualization of the environments and their changes going from $(NH_4)_2WS_4$ to $(CH_3NH_3)_2WS_4$.

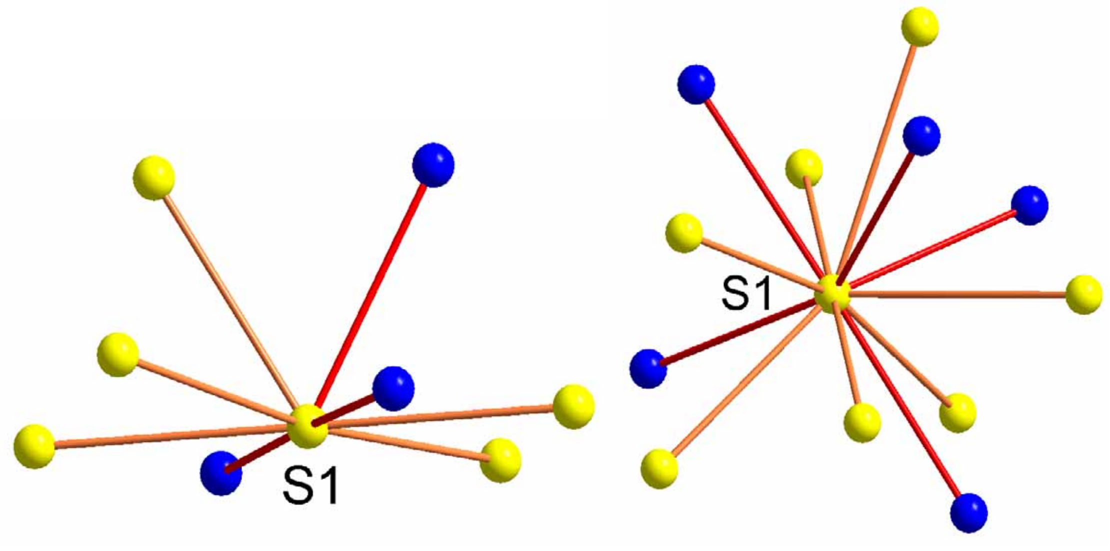
These figures support the assignment of the S-sites to the ^{33}S MAS NMR signals, i.e., the S2 atom is most affected when one H atom is substituted by a CH_3 group.



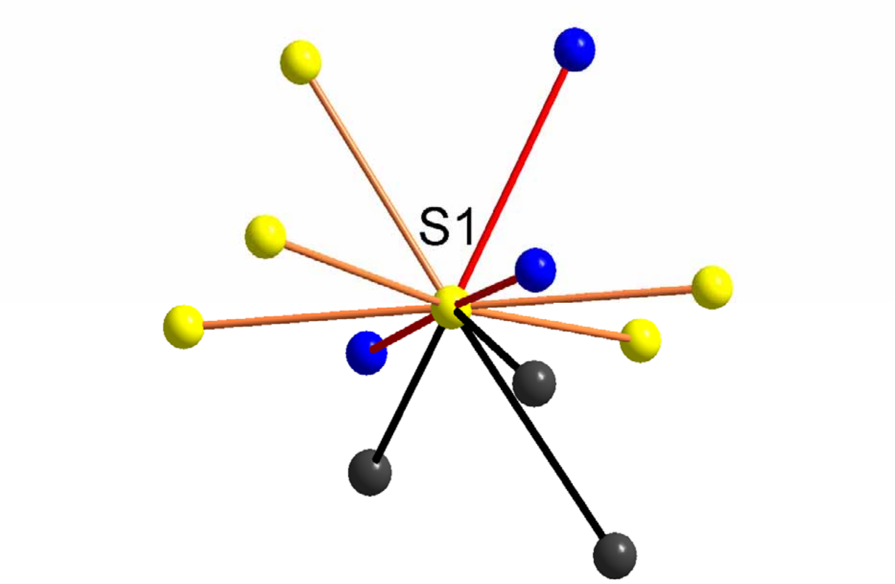
The environment around the S1 and S2 atoms in the structure of $(NH_4)_2WS_4$.



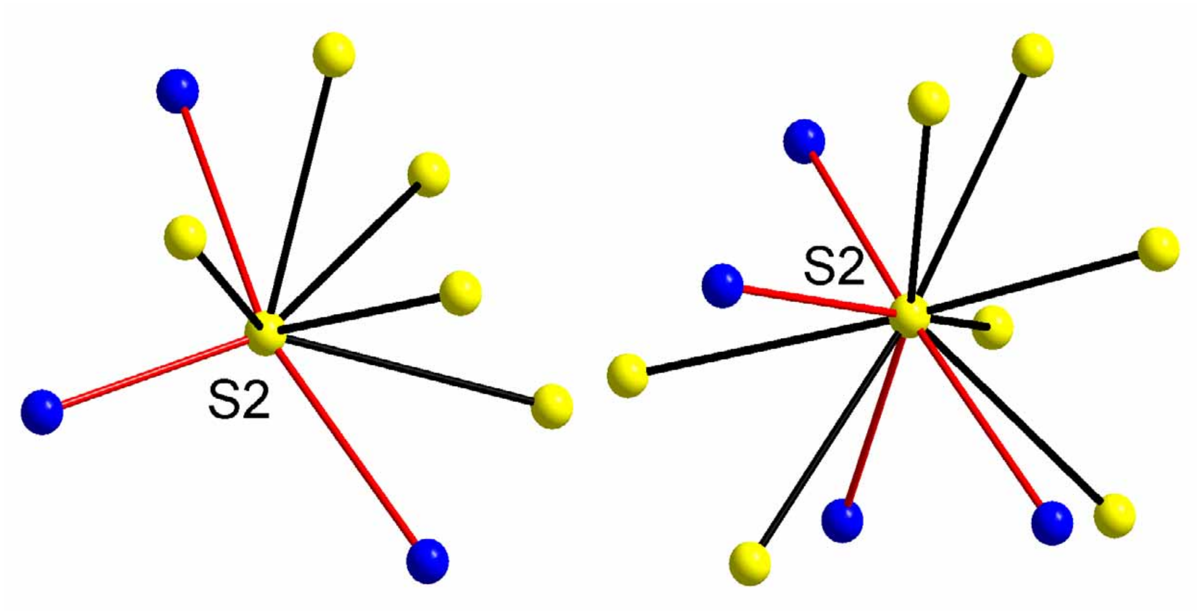
The environment around the S1 and S2 atoms in the structure of $(CH_3NH_3)_2WS_4$.



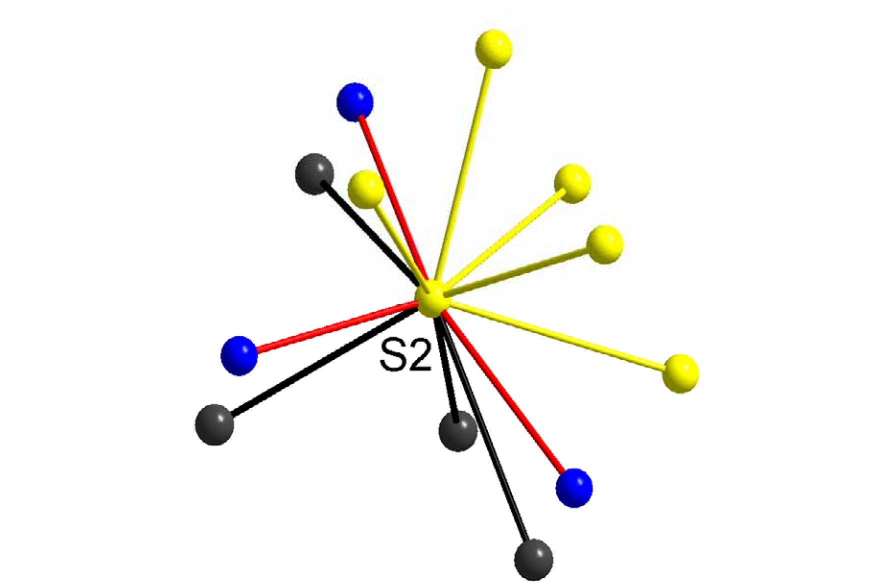
S1 environment in the $(CH_3NH_3)_2WS_4$ compound (left) and in $NH_4)_2WS_4$ (right)



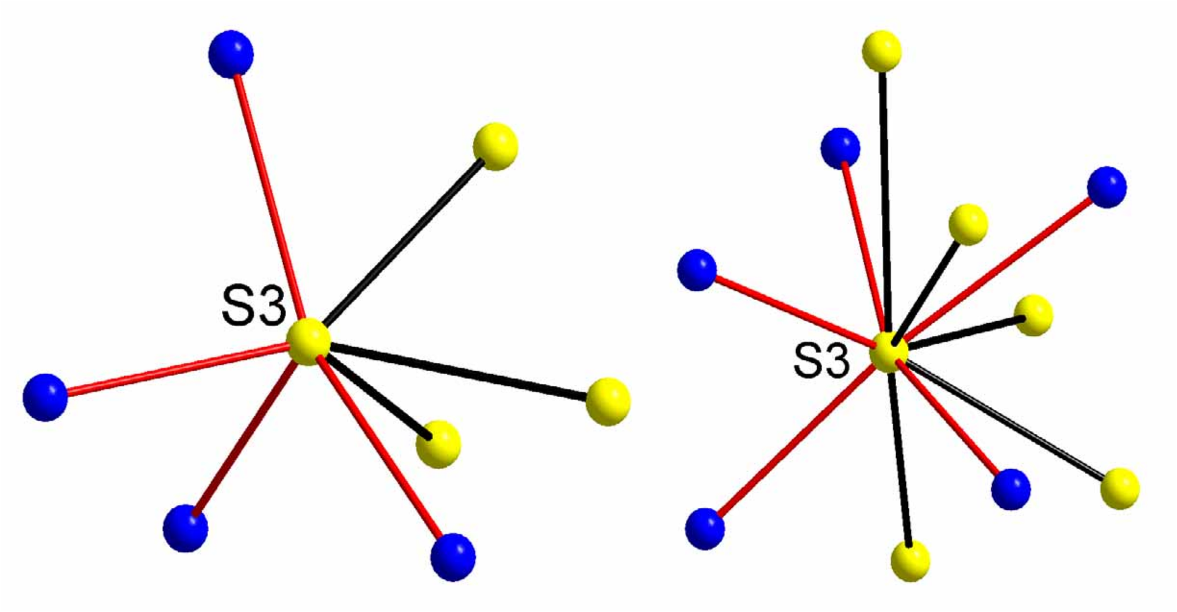
S1 in $(CH_3NH_3)_2WS_4$ including S-C contacts up to 4 Å



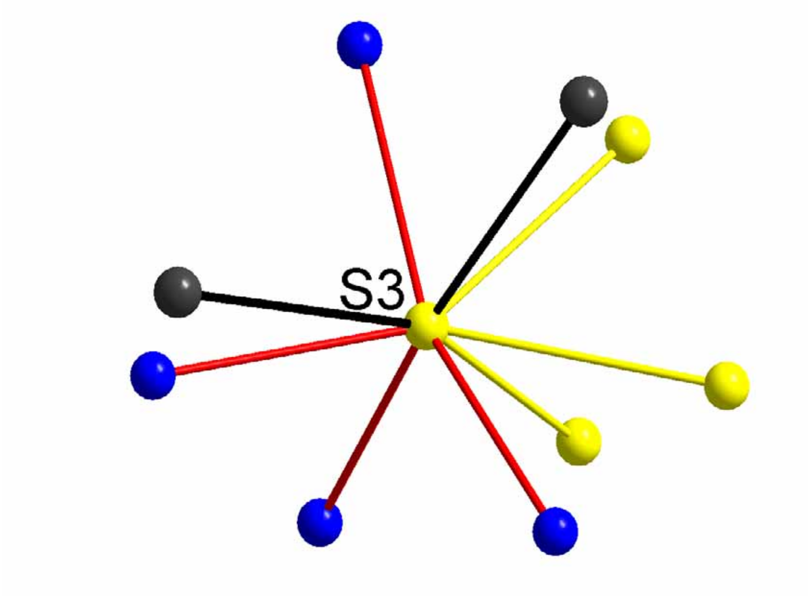
S2 in $(CH_3NH_3)_2WS_4$ (left) and in $(NH_4)_2WS_4$ (right)



S2 in $(CH_3NH_3)_2WS_4$ with C atoms up to 4 Å



S3 in $(CH_3NH_3)_2WS_4$ (left) and in $(NH_4)_2WS_4$ (right)



S3 in $(CH_3NH_3)_2WS_4$ with C up to 4 Å

Comparison of the ^{33}S chemical shift tensors with the ^{77}Se and ^{17}O tensors for $(NH_4)_2WSe_4$ and K_2WO_4

It is of interest to compare the anisotropic and isotropic ^{33}S chemical shift parameters (and their assignments) for the three nonequivalent S atoms in the WS_4^{2-} ion of (I) and (II) determined in the present study with the corresponding parameters recently reported for the three nonequivalent ^{77}Se (spin $I = 1/2$) atoms in the WSe_4^{2-} ion of $(NH_4)_2WSe_4$,[3] which is isostructural (*Pnma*)[4] with (I) and (II). In this report[3] the ^{77}Se chemical shift tensors are presented using the convention of principal axis components (δ_{xx}, δ_{yy}, δ_{zz}) of the tensors. For a convenient comparison of these data with the parameters listed for (I) and (II) in Table 1 of this work, we have converted these principal axis components for the tensors to the representation used here (δ_σ, η_σ, δ_{iso}) employing the definitions given in the Experimental Section, Eqs. (1) – (4), of the full article. The converted data are summarized below in Table 1 of this Supporting Information along with the parameters for (I) and (II). Most importantly, this has allowed us to assign the experimental data reported for $(NH_4)_2WSe_4$ in rows **15b** and **15c** of Table 3 in reference[3] to the Se(3) and Se(2) sites,

Table 1. Comparison of the chemical shift anisotropic and isotropic parameters (δ_σ, η_σ, δ_{iso}) for ^{33}S in $(CH_3NH_3)_2WS_4$ (I) and $(NH_4)_2WS_4$ (II) determined in the present study with the corresponding ^{77}Se and ^{17}O parameters earlier reported for $(NH_4)_2WSe_4$[3] and K_2WO_4,[6] respectively (see text).

Compound/sites	δ_σ (ppm)	η_σ	δ_{iso} (ppm)	Ref.
$(CH_3NH_3)_2WS_4$ (I)				
S(1,1)	401	0.11	545.3	This work
S(2)	344	0.10	473.1	–
S(3)	383	0.25	491.5	–
$(NH_4)_2WS_4$ (II)				
S(1,1)	389	0.16	542.3	5
S(2)	380	0.05	495.8	–
S(3)	396	0.35	518.7	–
$(NH_4)_2WSe_4$				
Se(1,1)	926 (398)[a]	0.03	1338 (562)[b]	3
Se(2)	864 (372)[a]	0.01	1155 (485)[b]	–
Se(3)	892 (384)[a]	0.32	1256 (527)[b]	–
K_2WO_4				
O(1,1)	220	0.15	437	6
O(2)	214	0.30	422	–
O(3)	227	0.22	429	–

[a] Value in parenthesis is the experimental value scaled by a factor of 0.43 (see text).
[b] Value in parenthesis is the experimental value scaled by a factor of 0.42 (see text).

respectively, as reported in the crystal structure work.[4] These sites are identical to the convention used for the S(3) and S(2) sites in the crystal structure of (I)[1] and thus for both (I) and (II) in Table 1. With this assignment it is seen from Table 1 that not only the ^{77}Se isotropic chemical shifts (δ_{iso}) but also the highly precise ^{77}Se chemical shift anisotropy (CSA) parameters (δ_σ and η_σ) for $(NH_4)_2WSe_4$ follow the same order as do these parameters for the S(1,1), S(2), and S(3) sites in (I) and (II), except for S(3) in (II) for which the δ_σ value is slightly larger than δ_σ for S(1,1). For $(NH_4)_2WSe_4$ we note that the three $\delta_\sigma(^{77}\mathrm{Se})$ values are about a factor 2 larger than the corresponding ^{33}S values for (I) and (II), in agreement with the general observation of a larger span in chemical shift for the heavier atom. To obtain a "closer" comparison of the ^{33}S and ^{77}Se parameters (δ_σ and δ_{iso}) for $(NH_4)_2WS_4$ (II) and $(NH_4)_2WSe_4$ we have calculated scaling factors for $\delta_\sigma(^{77}\mathrm{Se})$ and $\delta_{\mathrm{iso}}(^{77}\mathrm{Se})$ by taking ratios of the average values for the three δ_σ and δ_{iso} values for the two compounds. For $\delta_\sigma(^{77}\mathrm{Se})$ this gives a scaling factor of 0.43 and for $\delta_{\mathrm{iso}}(^{77}\mathrm{Se})$ a scaling factor of 0.42 is obtained. The corresponding calculated "reduced $\delta_\sigma(^{77}\mathrm{Se})$" and "reduced $\delta_{\mathrm{iso}}(^{77}\mathrm{Se})$" values are shown in parentheses in Table 1 next to the real values. These values show good similarities with the values for the corresponding ^{33}S parameters in (I) and (II).

Finally, following the comparison of the ^{77}Se and ^{33}S chemical shift parameters, it also seems of interest to extend the comparison to the 25-years old ^{17}O isotropic and anisotropic chemical shift data determined for this quadrupole (spin $I = 5/2$) in a sample of ^{17}O-enriched K_2WO_4.[6] It is noted that despite the fact that K_2WO_4 is *not* isostructural to (I), (II), and $(NH_4)_2WSe_4$, its crystal structure (*C*2/*m*) is very similar to those structures, i.e., with two nonequivalent oxygens (O(2) and O(3)) positioned on a mirror plane and two equivalent oxygens (O(1)) outside this plane for the WO_4^{2-} ion.[7] This structure is also reflected by its ^{17}O MAS NMR spectrum,[6] which shows an appearance similar to those for the ^{33}S and ^{77}Se spectra of the ammonium WS_4^{2-} and WSe_4^{2-} salts, respectively. The ^{17}O principal axis components reported for the three ^{17}O chemical shift tensors[6] have been converted to the (δ_σ, η_σ, δ_{iso}) representation (Table 1), similar to the ^{77}Se chemical shift data, and are arranged in Table 1 (Supporting Information) according to the same order for $\delta_{\mathrm{iso}}(^{17}\mathrm{O})$ as observed for $\delta_{\mathrm{iso}}(^{33}\mathrm{S})$ and $\delta_{\mathrm{iso}}(^{77}\mathrm{Se})$, and the oxygens then numbered similar to S and Se atoms; (it is noted that this numbering does not correspond to that used for the crystal structure of K_2WO_4.[7] The trend observed for the ^{17}O parameters in Table 1 generally conform to the discussion above for the ^{33}S and ^{77}Se parameters. In particular, the magnitudes observed for $\delta_\sigma(^{17}\mathrm{O})$ follow the order $\delta_\sigma(^{17}\mathrm{O}) < \delta_\sigma(^{33}\mathrm{S}) < \delta_\sigma(^{77}\mathrm{Se})$ in accordance with the heavy-atom effect observed above for $\delta_\sigma(^{33}\mathrm{S})$ and $\delta_\sigma(^{77}\mathrm{Se})$ in the WS_4^{2-} and WSe_4^{2-} ions. However, since the three sets of $\delta_\sigma(^{17}\mathrm{O})$ and $\eta_\sigma(^{17}\mathrm{O})$ values for the three nonequivalent oxygens are quite similar it is noted that the precision of these data is most likely somewhat lower compared to the other data in Table 1 as a result of the method used at that time for extraction of the chemical shift anisotropies (the method of Herzfeld and Berger[8]).[6] Although the data for K_2WO_4 represent the first reported example of ^{17}O chemical shift anisotropies it is unfortunate that in this very early study[6] it was not possible to determine the magnitudes of the small ^{17}O quadrupole coupling parameters (C_Q, η_Q) for the three ^{17}O sites in K_2WO_4. Clearly it would have been of interest to compare these parameters with the ^{33}S quadrupole coupling data determined in the present study for the corresponding WS_4^{2-} ions.

References

1 B. R. Srinivasan, C. Näther and W. Bensch, *Acta Cryst.* 2008, **E64**, m296.

2 B. R. Srinivasan, M. Poisot, C. Näther and W. Bensch, *Acta Cryst.* 2004, **E60**, i136.

3 B. A. Demko, K. Eichele and R. E. Wasylishen, *J. Phys. Chem. A*, 2006, **110**, 13537.

4 A. Müller, B. Krebs and H. Beyer, *Z. Naturforsch.* 1968, **23B**, 1537.

5 H. J. Jakobsen, A. R. Hove, H. Bildsøe, J. Skibsted and M. Brorson, *Chem. Commun.* **2007**, 1629.

6 S. Schramm and E. Oldfield, *J. Am. Chem. Soc.* 1984, **106**, 2502.

7 A. S. Koster, F. X. N. M. Kools and G. D. Rieck, *Acta Cryst.* 1969, **B25**, 1704.

8 J. Herzfeld and A. E. Berger, *J. Chem. Phys.* 1980, **73**, 6021.