NMR Investigations of ^{17}O, ^{33}S, ^{95}Mo, and ^{97}Mo in Thiomolybdates

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Z. Naturforsch. **35a**, 226–229 (1980); received December 24, 1979

NMR investigations of ^{17}O, ^{33}S, ^{95}Mo, and ^{97}Mo have been used to elucidate the existence and the behaviour of the oxothiomolybdate species, $MoO_{4-n}S_n^{2-}$ ($n = 0, 1, 2, 3, 4$) in aqueous solution. Very large chemical shifts and surprisingly narrow lines have been found for these nuclei in the different species.

Introduction

In the thiomolybdates $MoO_{4-n}S_n^{2-}$ ($n = 0, 1, 2, 3, 4$), four different nuclei can give rise to NMR signals: ^{17}O, ^{33}S, ^{95}Mo and ^{97}Mo. All of those are quadrupolar nuclei with relatively low NMR receptivity. The study of different nuclei in one single compound yields more information with respect to structure and ligand exchange. Second, experiments of this type can show the advantages and limits of the NMR signals of a certain nucleus in the compound investigated.

Most recently ^{95}Mo NMR was used to study simple and low molecular weight compounds [1–4], and it was possible to identify different molybdenum (VI) chalcogenide anions in aqueous solutions [5]. The rather narrow linewidth of the ^{95}Mo NMR signal in MoS_4^{2-} allowed measurements of the small ^{32}S-^{34}S isotope effect [6]. Because the quadrupole moment of ^{97}Mo is much larger than that of ^{95}Mo [1, 2, 7], ^{97}Mo NMR measurements will allow the acquisition of more reliable data about the natural linewidths and the quadrupole relaxation in the thiomolybdates.

Furthermore, it is known from time-dependent ^{95}Mo NMR experiments, that some of the thiomolybdates will decompose in aqueous solution, so that at last no ^{95}Mo signal or only that due to the MoO_4^{2-} species can be obtained. If one takes into account the rather small linewidths of ^{17}O in MoO_4^{2-} of a few Hz [8–10] and the wide application range ^{17}O NMR has reached until now [11–16], it should perhaps be possible to get further information from ^{17}O measurements of the thiomolybdates.

In analogy to the ^{17}O NMR measurements, ^{33}S investigations are possible for the thiomolybdates, although ^{33}S NMR plays a rather unimportant role in chemistry [9, 17, 18], because the ^{33}S NMR signal is rather weak and in most cases broad signals seem to dominate.

Experimental

The NMR measurements of the nuclei ^{17}O, ^{33}S, ^{95}Mo and ^{97}Mo were performed at (299 ± 2) K with a multinuclei Bruker pulse spectrometer SXP 4–100 in a magnetic field of 2.11 T, which was externally stabilized by a ^{1}H-NMR stabilization unit. For the described investigations it was very essential, that within short times the NMR signals of the different nuclei could be observed in the same sample. Some data, which are important for these nuclei are given in Table 1. For the measurements non-rotating cylindrical samples with 10 mm outer diameter were used. The chemical shift is reported as $\delta = (\nu_{\text{sample}}/\nu_{\text{ref}}) - 1$, where the reference sample for the different nuclei is described in the text.

The molybdenum (VI) thiomolybdates were prepared as described earlier in the literature: $(NH_4)_2MoO_2S_2$ [20], K_3MoOS_3Cl [21], K_2MoS_4 [20]. The purity of the compounds prepared was carefully checked by comparison of the electronic and IR spectra with the values reported in [22]. Generally the molybdenum complexes were dissolved in water, which had been flushed by argon prior to the addition of the solid compound.

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Table 1. Important NMR parameters of the nuclei ^{17}O, ^{33}S, ^{95}Mo and ^{97}Mo. The quadrupole moments are from Ref. [19], ^{17}O and ^{33}S, and Ref. [7], ^{95}Mo and ^{97}Mo.

Nucleus	Natural abundance in %	Spin	Quadrupole moment in 10^{-28} m^2	Larmor frequency at 2.11 T	Solution	Receptivity (Proton = 1)
^{17}O [a]	0.037	5/2	– 0.026	12.20 MHz	0.25 M K_2MoO_4 in H_2O	$9.8 \cdot 10^{-8}$
^{33}S	0.76	3/2	– 0.055	6.91 MHz	0.25 M K_2MoS_4 in H_2O	$1.6 \cdot 10^{-7}$
^{95}Mo	15.72	5/2	– 0.019	5.87 MHz	1 M K_2MoO_4 in H_2O	$4.6 \cdot 10^{-6}$
^{97}Mo	9.60	5/2	0. 102	5.99 MHz	1 M K_2MoO_4 in H_2O	$3.0 \cdot 10^{-6}$

[a] This signal was observed in a sample with 10% ^{17}O.

Results and Discussion

Some chemical shift data of ^{95}Mo in molybdates and thiomolybdates have been already reported earlier [3 – 5] and are summarized together with the new results in Table 2. There is an increase in the Larmor frequency of ^{95}Mo of about 500 to 600 ppm if one oxygen atom is substituted by a sulfur ligand in the thiomolybdates. The linewidths of the ^{95}Mo signals are relatively small and might still be falsified by magnetic field inhomogeneities. Therefore we used the NMR signal of ^{97}Mo, which has a quadrupole moment 11 times stronger than that of ^{95}Mo. If quadrupole interaction is an essential relaxation mechanism for the molybdates and thiomolybdates [1, 2], the ^{97}Mo NMR signals must be much broader than the ^{95}Mo signals, and for these linewidths the magnetic field inhomogeneity plays only a minor role. The observed chemical shifts and linewidths for ^{97}Mo are also collected in Table 2. The results of the chemical shift agree well for both molybdenum isotopes. The linewidths of the ^{97}Mo signals are indeed much broader than for ^{95}Mo. In the case of the MoO_3S^{2-} species the signal linewidth must be extremely broadened, thus no signal could be observed for this compound. But this fact is already indicated by the linewidth of ^{95}Mo in this monothiomolybdate, from which a linewidth of about 1 kHz for ^{97}Mo can be predicted. Such a broad signal can only be detected with extreme difficulties because 1) of the low sensitivity of the ^{97}Mo signal, and 2), because of the low concentration of the samples studied. The quadrupole interaction in MoS_4^{2-} seems to be smaller than in the tetra-oxo-species MoO_4^{2-}. This is somewhat surprising, but it allowed us to observe the rather small ^{32}S-^{34}S isotope effect of the ^{95}Mo NMR signal in MoS_4^{2-} [6]. Because some of the thiomolybdate samples are partially unstable in solution, NMR investigations of ^{95}Mo and ^{97}Mo are rather useful for recording the

Table 2. Chemical shift and linewidth data of ^{95}Mo and ^{97}Mo in the thiomolybdates: $MoO_{4-n}S_n^{2-}$ (n = 0, 1, 2, 3, 4) in H_2O relative to the molybdate ion MoO_4^{2-} at infinite dilution in H_2O.

Aqueous solution of	Compound	^{95}Mo		^{97}Mo	
		Chemical shift in ppm	Linewidths [a] in Hz	Chemical shift in ppm	Linewidths in Hz
K_2MoO_4, infinitely dilute	MoO_4^{2-}	0	0.5	0	35
$(NH_4)_2MoO_2S_2$, 0.5 molal	MoO_3S^{2-}	497(1)	10	—	—
$(NH_4)_2MoO_2S_2$, 0.5 molal	$MoO_2S_2^{2-}$	1067(1)	2.8	1064(2)	85
K_3MoOS_3Cl, 0.4 molal	MoO_3S^{2-}	1654(1)	0.7	1651(2)	35
K_2MoS_4, 0.5 molal	MoS_4^{2-}	2259(1)	0.3	2259(2)	25

[a] For rotating samples.

actual state of the sample. This is very favorable if the residual nuclei of these compounds could be also observed and assigned to the different species. We also detected the NMR signal of ^{17}O in an approx. 1 molal solution of $(NH_4)_2MoO_2S_2$ in H_2O, which was enriched in ^{17}O to about 10%. A small amount of ammonia was added to get a slower decomposition of the sample. In addition to the very strong ^{17}O signal of the solvent three signals could be observed for the several thiomolybdates in a freshly prepared sample (Table 3). At the same time, for this sample, four ^{95}Mo signals were observed due to the different species $MoO_{4-n}S_n^{2-}$, $n = 0, 1, 2, 3$. Comparing the time dependence of the ^{17}O and ^{95}Mo signals over a few hours, the different ^{17}O signals could be assigned to the $MoO_{4-n}S_n^{2-}$, $n = 0, 1, 2$ ions. Only for the thiomolybdate $MoOS_3^{2-}$ ion no ^{17}O signal was detectable, although this ion was also present in the solution as demonstrated by the corresponding ^{95}Mo species. It is quite clear, that the ^{17}O signal of $MoOS_3^{2-}$ is difficult to observe because for the same number of each thiomolybdate species the signal of the $MoO_2S_2^{2-}$ ion is two and that of the MoO_4^{2-} ion is four times stronger than the signal in the $MoOS_3^{2-}$. Furthermore, due to the decomposition of the sample the intensity of the ^{95}Mo signal of $MoO_2S_2^{2-}$ and $MoOS_3^{2-}$ decrease, so that after one day only a ^{95}Mo signal of MoO_4^{2-} and a very weak signal of MoO_3S^{2-} is left. A few hours after the preparation of the sample new ^{17}O signals could be observed, which increased with time. For these signals no corresponding ^{95}Mo signals could be detected. Most likely these new signals stem from some polymolybdates formed in solution, which are known to yield rather broad signals.

We did not try to assign these ^{17}O signals because at present only a few data are available on the decomposition of $MoO_{4-n}S_4^{2-}$ in solution. The signal of ^{17}O in the MoO_4^{2-} ion in this solution is rather broad compared with the linewidth in a pure molybdate solution of a few Hz. The other linewidths of the thiomolybdates are comparable in magnitude to the water signal. As already observed for the ^{95}Mo and ^{97}Mo signals, there is a nearly constant change in chemical shift in the ^{17}O signals if an oxygen atom is substituted by a sulfur atom. The chemical shift of ^{17}O is about one order of magnitude smaller than that of the ^{95}Mo signal. The chemical shift of ^{17}O between SO_4^{2-} and $S_2O_3^{2-}$ is nearly the same as that measured between different thiomolybdates [9].

Table 3. Chemical shift and linewidth data of ^{17}O in the oxothiomolybdates $MoO_{4-n}S_n^{2-}$ ($n = 0, 1, 2$), which occur in a solution of $(NH_4)_2MoO_2S_2$ in H_2O (10% enriched in ^{17}O).

Compound	Chemical shift in ppm	Linewidth in Hz
H_2O	0	85
MoO_4^{2-}	532(3)	114
MoO_3S^{2-}	595(3)	80
$MoO_2S_2^{2-}$	646(2)	70

It is known, that the ^{95}Mo NMR linewidth is rather small in MoO_4^{2-} and also in MoS_4^{2-} [1 – 6], it is further known, that the ^{17}O linewidth in MoO_4^{2-} is also very small [8 – 10]. Consequently the NMR linewidth of ^{33}S in MoS_4^{2-} should not be too broad, as illustrated in Fig. 1 for a 0.1 molal $(NH_4)_2MoS_4$ solution. The chemical shift of this signal is 343(2) ppm to higher frequency relative to a 4 molal Cs_2SO_4 solution, the linewidth of a nonrotating sample was about 40 Hz. For the other thiomolybdates no ^{33}S NMR signals could be found. The signal, which we earlier assigned to the MoS_4^{2-} ion seems identical to a signal observed for the $S_2O_3^{2-}$ ion [9]. This could also be shown by an ^{17}O NMR measurement in a corresponding solution of MoS_4^{2-}.

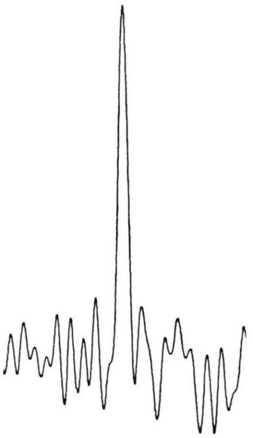

Fig. 1. ^{33}S NMR signal of a 0.1 molal solution of $(NH_4)_2MoS_4$ in H_2O in a nonrotating sample of 1.5 ml volume with a linewidth of 40 Hz. Experimental spectrum width: 20 kHz, number of pulses 108 000, measuring time 15 h, 1 k data points were accumulated, followed by 15 k points of zero-filling before Fourier transformation of 16 k data points.

By these experiments we were able to demonstrate, that in addition to ^{95}Mo NMR spectroscopy molybdates and thiomolybdate can be investigated by application of ^{97}Mo, ^{17}O and ^{33}S FT-NMR. Especially from the linewith of ^{97}Mo one obtains much more reliable data on the quadrupole relaxation in the thiomolybdates, whereas the chemical shifts remain the same. On the other hand, it is easier to detect ^{95}Mo NMR signals than ^{97}Mo signals, if the quadrupole relaxation can not be neglected. ^{17}O signals could show, that beside the $MoO_{4-n}S_n^{2-}$ ($n = 0, 1, 2, 3, 4$) compounds other decomposition products must exist in aqueous solution, which have not been indentified until now, and which were not detected by ^{95}Mo and ^{97}Mo NMR. Finally, similarly to the situation in MoO_4^{2-} which gives very narrow ^{17}O and ^{95}Mo NMR linewidth, the sharp ^{33}S and ^{95}Mo signals of MoS_4^{2-} indicate a symmetric electric field at the molybdenum and sulfur nucleus.

Acknowledgement

We thank Prof. H. Krüger for his support of this work and the Deutsche Forschungsgemeinschaft for their financial support.

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