NOTIZEN

Use of ^{95}Mo NMR for Identification of Molybdenum (VI) Chalcogenide Anions in Aqueous Solution

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^{95}Mo Fourier transform nuclear magnetic resonance studies were made on aqueous solutions of oxo thiomolybdates. Chemical shifts up to 2200 ppm were found for the different unambiguously assigned species $MoO_{4-n}S_n^{2-}$ ($n=0, 1, 2, 3, 4$).

Introduction

^{95}Mo NMR spectroscopy has been successfully employed in the investigation of the formation and properties of diamagnetic molybdenum complexes in solution as well as in the solid state[1–3]. Taking the molybdate anion, MoO_4^{2-}, as a reference, large chemical shifts up to 2000 ppm have been observed for the ^{95}Mo isotope upon changing the valence state of the metal from 0, +4 or +6.

A second interesting question with respect to the chemical shift of the ^{95}Mo resonance arises from the substitution of ligand atoms with different donor strength, such as oxygen, sulfur or selenium, at the molybdenum site within a given oxidation state and ligand field geometry.

The reaction in aqueous solution of H_2S and MoO_4^{2-} to form different oxothiomolybdates MoO_3S^{2-}, $MoO_2S_2^{2-}$ or $MoOS_3^{2-}$ has been the object of numerous studies by Bernard and Tridot[4] as well as Müller[5]. Although these anions exhibit distinct absorption maxima in their electronic spectra[5], the quantitative and qualitative analysis of solutions containing mixtures of the different molybdate species seems rather ambiguous due to overlap of several absorption bands in the region 280 to 460 nm. These difficulties can be easily overcome by ^{95}Mo NMR spectroscopy as demonstrated in this paper.

Experimental

^{95}Mo and ^{97}Mo Fourier transform NMR spectra were measured at 5.86 MHz and 5.99 MHz on a multinuclei Bruker spectrometer[1] at (299 ± 2) K. Nonrotating cylindrical samples of 10 mm diameter were used. Chemical shifts are reported as $\delta = (\nu_{\text{sample}}/\nu_0) - 1$, where ν_0 is the Larmor frequency of the ^{95}Mo signal in MoO_4^{2-} at infinite dilution in H_2O (Reference[1]).

The molybdenum (VI) chalcogenides were prepared according to the methods described in the literature: K_2MoO_3S (Ref.[6]), $(NH_4)_2MoO_2S_2$

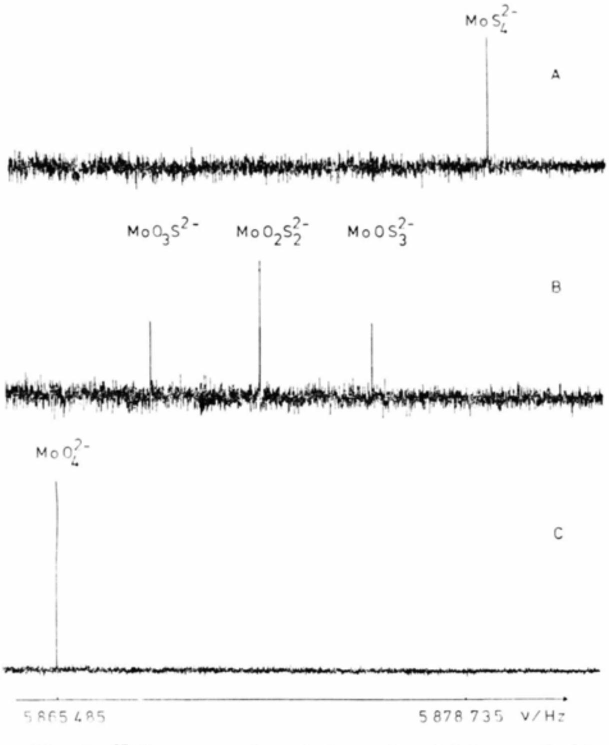

Fig. 1. ^{95}Mo spectra in solutions of molybdate and thiomolybdate in H_2O: A: 0.6 molal solution of K_2MoS_4 freshly prepared; B: 0.3 molal solution of $(NH_4)_2MoO_2S_2$ freshly prepared; C: 2.6 molal solution of K_2MoO_4. (The single line, which was found in an earlier work[2] and ascribed to the MoS_4^{2-} ion, was really the signal of the MoO_3S^{2-} species). Experimental parameters: experimental spectrum width: 20 kHz; pulse repetition frequency: 1 Hz; number of pulses: for A and B 850, for C 10; nonrotating cylindrical sample tubes with 1.5 ml sample volume were used. 4 K data points were accumulated followed by 4 K of zero-filling before Fourier-transformation.

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(Ref. [7]), Cs_2MoOS_3 (Ref. [8]), K_3MoOS_3Cl (Ref. [9]), K_2MoS_4 (Ref. [7]) and $(NH_4)_2MoS_4$ (Reference [7]). The purity of all the compounds prepared has been checked by comparison of the electronic and IR spectra with the values reported in Reference [5].

Results

In aqueous solution the different molybdate (VI) anions $MoO_{4-n}S_n^{2-}$ ($n = 0$, 1, 2, 3 and 4) exhibit well resolved ^{95}Mo signals as illustrated in Figure 1. Freshly prepared solutions of K_2MoS_4 or $(NH_4)_2MoS_4$ as well as Cs_2MoOS_3 and K_3MoOS_3Cl definitely show one single line within the measuring time (see Fig. 1. spectrum A), which allows unambiguous assignment for the two anions $MoOS_3^{2-}$ and MoS_4^{2-}. However, this is neither valid for the corresponding dithiomolybdate $MoO_2S_2^{2-}$ nor the monothiomolybdate MoO_3S^{2-}, which seem to decompose very rapidly under the conditions used (see Fig. 1, spectrum B). Thus after standing for about one hour, a 0.2 molal solution of $(NH_4)_2MoO_2S_2$ in water, pH 7, clearly shows four distinct lines at $-(0.7 \pm 1.0)$ ppm, (497 ± 1) ppm, (1067 ± 1) ppm and (1654 ± 1) ppm. The relative intensities of the four signals vary depending on time and pH. Generally the stability of the mono- and dithio species can be sufficiently enhanced by addition of the appropriate base raising the pH up to 10 or 11. From the chemical shifts determined in solutions of the stable thiomolybdates $MoOS_3^{2-}$ and MoS_4^{2-}, the four NMR signals described above can be easily attributed to MoO_4^{2-}, MoO_3S^{2-}, $MoO_2S_2^{2-}$ and $MoOS_3^{2-}$. For comparison the chemical shift of the tetrathio anion is measured to be (2259 ± 1) ppm.

The influence of different cations such as K^+, Cs^+ or NH_4^+ on the chemical shift of the molybdates investigated amounts to a few ppm as well as the effect of pH over the range of 7.5 to 11.5. The Larmor frequency decreases with increasing pH as already observed for the tetraoxo anion in aqueous solution [1]. The linewidth of all the ^{95}Mo NMR signals detected is caused by the inhomogeneity of the magnetic field. However, preliminary ^{97}Mo measurements of both $MoOS_3^{2-}$ and MoS_4^{2-} show linewidths of about 40 Hz, which are comparable to those for MoO_4^{2-}.

Substitution of a first oxygen atom by sulfur leads to a chemical shift of the ^{95}Mo NMR signal of 500 ppm to higher frequency for the monothio molybdate. Further replacement of the oxygen ligands adds 600 ppm for each oxygen atom. Similar effects have been reported for the ^{31}P NMR spectra of the $PO_{4-n}S_n^{3-}$ ($n = 0$, 1, 2, 3 and 4) series [10] and for the ^{55}Mn NMR spectra of $Mn(CO)_5X$ with X being Cl, Br or I (Reference [11]).

The investigations described in this paper clearly show that "inorganic" NMR spectroscopy may act as a rather powerful tool to study the properties of diamagnetic metal complexes in addition to the more common optical methods. This is mainly due to the fact that within a fixed oxidation state of the metal extremely large chemical shifts can be found depending on the donor strength of the ligand attached to the metal site. Although at present our NMR studies of diamagnetic molybdenum compounds are in a preliminary stadium, the results presented may be very interesting for future applications of ^{95}Mo NMR spectroscopy in more complicated systems such as molybdenum enzymes.

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