Use of ^{95}Mo NMR Spectroscopy as a New Approach to Structural Analysis of Diamagnetic Molybdenum Complexes

O. Lutz and A. Nolle
Physikalisches Institut der Universität Tübingen, 7400 Tübingen, Morgenstelle, Germany

and P. Kroneck
Fachbereich Biologie der Universität Konstanz, 7750 Konstanz, Germany

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Fourier Transform NMR measurements of ^{95}Mo and ^{97}Mo are reported for several molybdenum compounds in different oxidation states. Using the molybdate ion as a reference, chemical shifts from about +500 ppm to about −1900 ppm have been observed. Experimental parameters and a chemical shift scale are given.

I. Introduction

Molybdenum has been widely used as a redox-active catalyst both in chemical systems and the living cell[1]. Its catalytic versatility seems mainly due to the fact that it can be more or less readily stabilized in several different oxidation states ranging from 0 to +VI. Mononuclear and diamagnetic complexes have been isolated in the oxidation states 0, +IV and +VI, whereas paramagnetic species could be discovered by Electron Paramagnetic Resonance predominantly in the +V state[2]. Three major results of preceding NMR study on ^{95}Mo and ^{97}Mo[3] should be relevant for further analysis of molybdenum in chemical and biological systems. First, by applying the Fourier Transform technique millimolal concentrations of total molybdenum can be detected. Second, the NMR linewidth of the ^{95}Mo isotope is rather narrow in molecules where the metal is centered in a symmetric ligand field exhibiting a low electric field gradient. As already mentioned earlier[4–6], this effect is probably due to the small quadrupole moment of ^{95}Mo. And third, by comparison with measurements of ^{53}Cr[7] and ^{183}W[8] the range of chemical shifts covered by molybdenum can be estimated to be around 3000 ppm.

It has been a first aim of our present NMR study to find possible correlations between the chemical shift and

a) the oxidation state of the metal, and
b) the nature of ligands at the metal site within a given oxidation state and field geometry.

Again, as in[3], only complexes have been investigated with the molybdenum located in a site of low electric field gradient in order to avoid broadening of the NMR signal measured. Thus, a question for future experiments then would be the dependence of chemical shift and linewidth on the symmetry of the ligand field around the metal within a given series of molybdenum complexes in the same oxidation state.

In addition to the data obtained by high resolution NMR measurements with ^{1}H, ^{13}C or other nuclei[9–11], our results indicate that molybdenum NMR spectroscopy might give further structural information valuable for both chemical and biological purposes.

II. Experimental

^{95}Mo and ^{97}Mo NMR spectra were recorded as described in[3]. In a magnetic field of 2.11 T the Larmor frequency of ^{95}Mo is about 5.865 MHz, whereas for ^{97}Mo it is around 5.989 MHz. The tetrathiomolybdate, MoS_4^{2-}, and the octacyanomolybdate, $Mo(CN)_8^{4-}$, were observed in nonrotating sample tubes, whereas the hexacarbonyl complex was measured in a rotating tube.

All experiments were performed at a temperature of (299 ± 2) K. $Mo(CO)_6$ was obtained from Merck (Darmstadt, Germany) and used without further purification. K_2MoS_4 was a commercially available product from Pfaltz and Baur (Flushing, N. Y., USA) or it was prepared by simply flushing H_2S into an alkaline solution of potassium molybdate. Upon cooling of the deep red solution in an ice-bath, a microcrystalline red solid precipitated, which was recrystallized twice from water-aethanol. The elementary analysis of both the commercial as well as of the synthesized product revealed minor

Reprint requests to Prof. Dr. O. Lutz, Physikalisches Institut der Universität Tübingen, Morgenstelle, *D-7400 Tübingen.*

contaminations due to starting material or intermediate thiomolybdates, having not all four oxygen atoms replaced by sulfur. These impurities did not effect our NMR investigations as outlined in the text. $K_4Mo(CN)_8 \times 2\,H_2O$ was prepared according to van de Poel and Neumann[12] and recrystallized twice. Its purity was checked optically at 367.7 nm using an extinction coefficient of $170\,M^{-1}\,cm^{-1}$.

III. Results and Discussion

a) Molybdenum signals in a solution of K_2MoS_4 in H_2O

In solutions of the tetrathiomolybate with pH values varying from 7 to 12, two NMR signals can be resolved. One appears at exactly the same position as measured in a corresponding K_2MoO_4 solution and consequently was assigned to the MoO_4^{2-} ion. The second signal at higher frequency then must be due to the MoS_4^{2-} complex. No signals of intermediate thiomolybdate ions (see Experimental section) could be detected. The Larmor frequency in a 0.4 molal solution of K_2MoS_4 does not depend on the pH value, but at pH greater 12.5 no NMR signal due to MoS_4^{2-} can be observed any longer, which is probably caused by partial decomposition of the thiomolybdate at higher concentrations of OH^-. Exact chemical shifts and linewidths are summarized in the table.

b) Molybenum signals in a solution of $K_4Mo(CN)_8$ in H_2O

In the octacyano complex molybdenum is in the tetravalent oxidation state with both d-electrons paired, i. e. the metal is located in a strong ligand field by cubic symmetry[13]. The ^{95}Mo resonance has been observed in a 0.3 molal solution of $K_4Mo(CN)_8$ in water as shown in Fig. 1 and the table. Note the unusually large linewidth in comparison to the other molybdenum species studied, which indicates that the octacyanomolybdate is presumably not an ideal cube in solution.

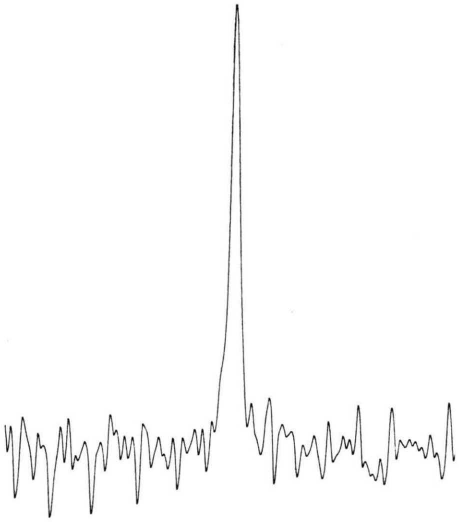

Fig. 1. Absorption signal of ^{95}Mo in a 0.3 molal solution of $K_4Mo(CN)_8$ in H_2O. Larmor frequency: 5.857 798 MHz; line width: 75 Hz; plotted spectrum width: 3 kHz; pulse repetition rate: 16.7 Hz; number of sweeps: 10000; accumulation time: 10 min; sample volume: 1 ml.

c) Molybdenum signals in solutions of $Mo(CO)_6$ in tetrahydrofuran

In the hexacarbonyl compound molybdenum is in the zero oxidation state. The NMR signals of both isotopes ^{95}Mo and ^{97}Mo have been detected in a solution of $Mo(CO)_6$ in tetrahydrofuran (THF). The NMR parameters of the ^{95}Mo resonance are compiled in the table. The linewidth of the corresponding ^{97}Mo signal in this solution is around 8 Hz, indicating that the natural linewidth of the ^{95}Mo isotope must be much smaller than the observed one.

Table 1. Results of NMR investigations of ^{95}Mo in diverse molybdenum complexes.

Solution	Concentration	Measuring time in min	Signal to noise ratio	Chemical shift in ppm *	Linewidth in Hz
K_2MoS_4 in H_2O	0.4 molal	35	10	496.1 (0.5)	5 (nonrotating)
$K_4Mo(CN)_8$ in H_2O	0.3 molal	10	25	−1309 (1)	75
$Mo(CO)_6$ in THF	0.08 molal	5	10	−1856.12 (22)	0.7

* All chemical shifts are referred to the MoO_4^{2-} ion at infinite dilution in H_2O; a positive shift means a shift to higher frequency.

In the hexacarbonyl complex the molybdenum nucleus seems to be in a highly symmetric environment similarly to the related chromium compound, where the ^{53}Cr signal has a chemical shift of comparable magnitude in THF [7].

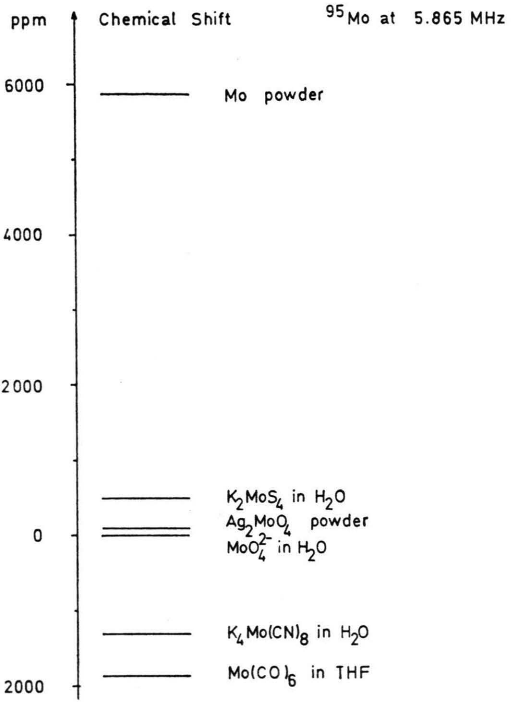

Fig. 2. Chemical shift and Knight shift of molybdenum. The shifts are referenced to the extrapolated frequency of the infinite dilution resonance of molybdenum in the molybdate ion in H_2O. A positive shift means a shift to higher frequency. The results of molybdenum powder and of Ag_2MoO_4 powder are given in Reference 3.

d) Conclusions

In Figure 2 all chemical shifts are plotted using MoO_4^{2-} as a reference [3]. Clearly $Mo(CO)_6$ in THF exhibits the lowest Larmor frequency of all molybdenum compounds investigated, whereas metallic molybdenum shows a value which is about 7705 ppm higher. Furthermore, as far as we can decide from these preliminary experiments, the Larmor frequency increases with increasing oxidation number of the metal, although one has to keep in mind that shifts of similar magnitude may be obtained within the +VI oxidation state upon substituting oxygen by a stronger donor ligand such as sulfur as demonstrated for the tetrathiomolybdate (Figure 2). Certainly a greater number of a variety of molybdenum complexes will have to be examined to elucidate the specific influence of the bound ligands on the chemical shift of the NMR signals within a given oxidation state and ligand field geometry. In the case of hexavalent tungsten it has already been established [8], that, upon variation of the ligands, chemical shifts can be achieved as large as those obtained by just scanning through a series of different oxidation states for molybdenum.

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