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The first direct detection of ^{99}Ru and ^{101}Ru NMR: Ru relaxation and the Ru- ^{17}O coupling constant in RuO_4 . Comparison with OsO_4 ^{a)}

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High resolution NMR spectra of ^{99}Ru and ^{101}Ru have been observed in CCl_4 solution of RuO_4 for the first time. The different NMR parameters (frequencies, linewidths, and T_1) have been measured for both isotopes. The ^{17}O spectra leads to $^1J_{^{17}\text{O}-^{99}\text{Ru}} = 23.4$ Hz. The dynamical behavior of RuO_4 and OsO_4 is compared using the measurement of T_1 and T_2 on ^{17}O , ^{99}Ru , ^{101}Ru , and ^{189}Os .

INTRODUCTION

Most of the stable magnetically active, isotopes of the Periodic Table have been observed by NMR. Only a few elements (1a) still endure such a physical study. Among these nuclei, Pd, Ru, and Ir play a very important role in inorganic chemistry and catalytic processes. We present in this paper the first high-resolution NMR observation of both Ruthenium isotopes ^{99}Ru and ^{101}Ru . Ruthenium possesses two magnetically active isotopes ^{99}Ru and ^{101}Ru (natural abundance: 12.72% and 17.07%, respectively) and previous studies^{2,3} were able to establish the magnetic moments (μ) and quadrupole moments (Q) of both isotopes

$$^{99}\text{Ru}: \mu = -0.6381(51) \mu_N; Q = 0.076(7) \text{ b},$$

$$^{101}\text{Ru}: \mu = -0.7152(60) \mu_N; Q = 0.44(4) \text{ b},$$

where μ_N represents the nuclear magneton value.

EXPERIMENTAL SECTION

All spectra have been recorded on a Bruker WM 250 spectrometer, by operating at a nominal field of 5.875 T, with 10 mm tube, without lock (probe temperature: 27°C). RuO_4 and OsO_4 were obtained from Alfa chemicals and used without further purification, except filtering out any solid particles from the solution. Final concentration of both samples was 1.02 M in CCl_4 . The tubes were sealed without any degassing cycle.

RESONANCE FREQUENCIES

A NMR spectrum has been obtained for both Ruthenium isotopes (Fig. 1). Due to the tetrahedral symmetry of the RuO_4 molecule, the resonance lines are very sharp (0.8 Hz for ^{99}Ru , 9 Hz for ^{101}Ru); nevertheless, the very small quadrupole moment of ^{99}Ru ^{2,3} suggest that reasonable linewidths could be obtained in ^{99}Ru NMR even for low symmetry environments. The requirements for such a situation have been recently met in the case of cluster type and RuII compounds.⁵ The exact resonance

frequencies for RuO_4 are respectively

$$^{99}\text{Ru}: \nu = 11.541\,356 \text{ MHz},$$

$$^{101}\text{Ru}: \nu = 12.935\,341 \text{ MHz},$$

with exactly the same field value. Taking into account the magnetic susceptibility difference between CCl_4 and H_2O , the water proton resonance is 250.134 741 MHz. These numbers, together with the proton water magnetic moment measured by Cohen and Taylor⁴ allow the determination of the magnetic constants for Ruthenium isotopes (Table I).

The difference between estimated¹ and experimental Ξ and μ values is large. This can be explained by the large range of the chemical shift (~ 6000 ppm) observed for the few compounds studied to date.⁵

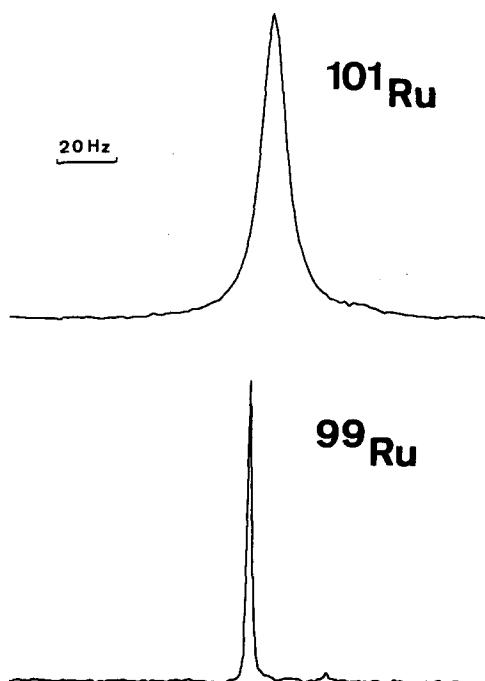


FIG. 1. ^{99}Ru and ^{101}Ru of RuO_4 in CCl_4 (1.02 M). ^{101}Ru : SW = 6000 Hz, 8 K points, 90° pulse, 200 scans. ^{99}Ru : SW = 1000 Hz, 2 K points, 90° pulse, 40 scans.

^{a)} Presented in part at GERM VI, Pont à Mousson, France, 11–13 March 1981.

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TABLE I. NMR parameters for ^{99}Ru and ^{101}Ru .

	γ (10^{-7} Rad T $^{-1}$ s $^{-1}$)	Ξ (MHz) ^a	μ/μ_N ^b	R_{13C} ^c
^{99}Ru	-1.2343	4.1640 ₇	-0.6442 ₉	0.83
^{101}Ru	-1.3834	5.1713 ₇	-0.7221 ₁	1.56

^a Ξ Resonance frequency in a field where the protons of TMS resonate at exactly 100 MHz.

^bThe Ru shielding coefficient for RuO_4 being unknown, the μ value for the bare nucleus is not obtainable.

^cRelative sensitivity with respect to ^{13}C .

RELAXATION

In view of going further in Ruthenium NMR parameters and gaining more informations on Ruthenium quadrupole coupling constant in RuO_4 , we have measured the spin-lattice relaxation times of both isotopes. At 27°C, using the inversion-recovery method⁶ we find the following T_1 values:

$$^{99}\text{Ru}: 0.98 \text{ s},$$

$$^{101}\text{Ru}: 0.033 \text{ s}.$$

In the extreme narrowing case, these T_1 values lead to a linewidth of 0.3 Hz for ^{99}Ru and 9.7 Hz for ^{101}Ru . If the ^{101}Ru calculated halfwidth value does fit the experimental one, the ^{99}Ru value is smaller than the measured width, due certainly to magnetic field inhomogeneities. These narrow lines make ^{99}Ru an ideal candidate for high-resolution studies despite its lower sensitivity compared to ^{101}Ru (see Table I). From the T_1 and spin quantum values (*Vide infra*) one can get the ratio $^{101}\text{Q}/^{99}\text{Q} = 5.45$ which closely parallels the published^{2,3} values ($^{101}\text{Q}/^{99}\text{Q} = 5.97$).

It must be noted that the tetrahedral environment around the Ruthenium site in RuO_4 should eliminate any quadrupolar relaxation pathway for the Ruthenium nucleus. Nevertheless, molecular collisions and nonsymmetrical vibrations do create a fluctuating electric field gradient along the Ru-O bond. To our knowledge, there is no theoretical treatment allowing a precise determination of the fluctuating quadrupole coupling constant in such a case.

^{17}O NMR OF RuO_4

The ^{17}O spectrum of RuO_4 is shown in Fig. 2. It consists of a central peak at +1106 ppm from H_2O and a four line pattern. A Gaussian deconvolution of the corresponding FID clearly shows a sextet fine structure which implies a spin quantum value $I = \frac{5}{2}$ for both Ruthenium isotopes. Figure 2(b) allows to discriminate between the ^{99}Ru and ^{101}Ru contributions to the fine structure; the ^{101}Ru satellites are broader than the corresponding ^{99}Ru lines, due to the larger quadrupole moment of ^{101}Ru , and therefore give the plateau-like structure. The one bond oxygen-17-Ruthenium-99 coupling constant deduced from the splitting is 23.4 Hz, leading to a reduced coupling constant $K_{17\text{O}-^{99}\text{Ru}} = 31.15 \times 10^{20} \text{ NA}^{-2} \text{ m}^{-3}$. This value is very close to that obtained for MoO_4^{2-} which is equal to: $K_{17\text{O}-^{95}\text{Mo}}$

$= 38.0 \times 10^{20} \text{ NA}^{-2} \text{ m}^{-3}$. This fact shows the similarity of the bonds between Mo-O and Ru-O. A careful determination of the relative intensities of the central peak with respect to the sum of the (sharp and broad) satellite structure leads to a 2.3/1 ratio which corresponds to the sum of the respective natural abundance of ^{99}Ru and ^{101}Ru relative to ^{100}Ru (central line). The spin-lattice relaxation time of ^{17}O , measured with the inversion recovery method, is equal to 0.1 s. This value permits the calculation of the ^{17}O quadrupole coupling constant, as for MoO_4^{2-} using the following parameters:

(i) The radius of the equivalent sphere estimated from the unit cell volume⁸ and from the number of molecules per unit cell: 2.18 Å.

(ii) The viscosity of CCl_4 : 0.843 cP.

One then gets a τ_c value of 8.3×10^{-12} s and an ^{17}O quadrupole coupling constant of 1.12 MHz which closely fits the value for MoO_4^{2-} , 720 kHz.

COMPARISON OF RuO_4 AND OsO_4 MOLECULAR DYNAMICS

In order to compare the Ruthenium and Osmium 189 quadrupole moments, we have measured the ^{189}Os T_1 value of a 1.02 M CCl_4 solution of OsO_4 . A linewidth determination of the Os resonance gives $T_1 = 370 \times 10^{-6}$ s a result which is close to the measurement of Sahm and Schwenk⁹ for molten OsO_4 . Since the corresponding bond lengths differ by only some tenths of angstroms, one can reasonably assume that τ_c and the fluctuating field gradients are nearly identical in RuO_4 and OsO_4 .^{8,10} Thus a straightforward comparison of ^{189}Os and ^{101}Ru quadrupole moments values can be obtained via

$$T_1^{-1} = \frac{3\pi^2}{10} \times \frac{(2I+3)}{I^2(2I-1)} \left(\frac{e^2 q Q}{h} \right)^2 \tau_c$$

and

$$Q_{184\text{Os}}/Q_{101\text{Ru}} = 4.63.$$

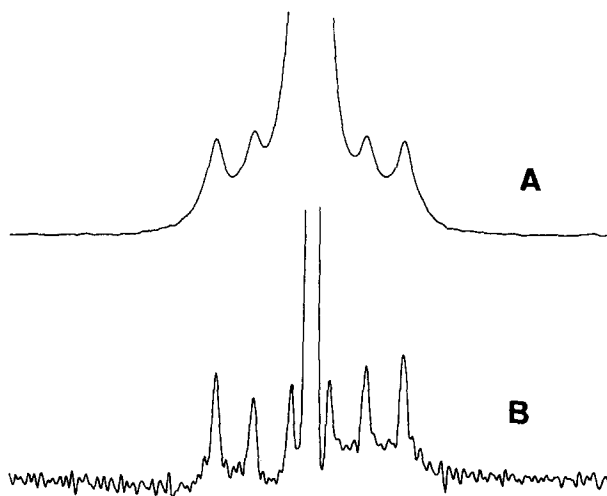


FIG. 2. ^{17}O spectrum of RuO_4 in CCl_4 (1.02 M). (a) normal spectrum; (b) with Gaussian filtering. Note the slight isotope shift of 0.02 ppm.

From published results [Ref. 1(a) p. 225, and Refs. 2 and 3] this ratio should be equal to 1.73. If one excludes the difference as arising from too imprecise Q values, then, the proposed microdynamical model could be very far from reality. To check the molecular dynamics of OsO_4 , we have measured the ^{17}O T_1 of the CCl_4 solution and thus got a T_1 value of 0.13 s (RuO_4 : 0.10 s). A similar model to the one used for RuO_4 (with a 2.21 Å value¹⁰ for the radius of the equivalent sphere) gives a τ_c of 8.7×10^{-12} s and a quadrupole coupling constant of 967 kHz. The reorientational motion of the Ru–O and Os–O bond vector in CCl_4 is then comparable and the discrepancy found between the ($Q_{^{183}\text{Os}}/Q_{^{101}\text{Ru}}$) ratio comes from a different fluctuating field gradient at the metal site.

One may think to possible associations between RuO_4 or OsO_4 molecules. However, the similarity of the ^{17}O relaxation time between these two molecules and MoO_4^{2-} ⁷ does not favor this hypothesis. The literature confirms the fact that OsO_4 behaves as a nonassociated substance in CCl_4 and H_2O .¹¹ To convince ourselves that no associations were involved, we have performed the ^{17}O NMR spectra of OsO_4 in benzene at the same concentration. A very sharp signal similar to those obtained in CCl_4 is observed with a similar relaxation time. We have tried to detect the ^{189}Os resonance, but we fail because the linewidth is probably too large. The discrepancy between the two values of the ratio $Q_{^{189}\text{Os}}/Q_{^{101}\text{Ru}}$ and the influence of the solvent on the ^{189}Os resonance may be explained in terms of a greater sensitivity of the ^{189}Os outer electronic sphere to molecular collisions in solution, since, in contrast with Ruthenium, the f orbitals may play an important role for the Osmium nucleus. As an example, it has been shown¹² that these two compounds behave quite differently when dissolved in water.

CONCLUSION

In view of the spectral characteristics found, Ruthenium high resolution NMR seems to be very promising.

The availability of two different isotopes with not too high a quadrupole moment should initiate molecular dynamics studies on model compounds. On the other hand, ^{99}Ru will certainly become an invaluable structural probe in inorganic chemistry because of its sharp resonance lines even in nonsymmetrical environments and its large chemical shift range which should allow study of subtle electronic changes at the Ruthenium moiety. We propose to adopt RuO_4 in CCl_4 as the reference compound, as commercial solutions are readily available. We are investigating thoroughly the chemical applications (chemical shift scale, coupling constants, etc...) of ^{99}Ru NMR in our laboratories.⁵

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