Solid-State Tungsten-183 Nuclear Magnetic Resonance Spectroscopy
C. T. G. Knight,* G. L. Turner,† R. J. Kirkpatrick,§ and Eric Oldfield*‡

School of Chemical Sciences, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801
Department of Geology, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

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We report the first direct observation of the 183W NMR signals of a variety of tungsten-containing solids, using a relatively high magnetic field (8.45 T) together with the technique of "magic angle" sample spinning (MASS).

Although the utility of 183W NMR has been clearly demonstrated in solution, it as, for example, in determining the structures of isopolystungstates, or "Keggin" cluster compounds, the successful application of high-resolution 183W MASS NMR to solid compounds has not been reported. This is at first sight surprising since it appears from the variety of magnetic properties of the 183W nucleus (I = 7/2, abundance = 14.4%, g = 4.1 MHz) and is almost certainly due to exceedingly long spin–lattice relaxation times. Since the application of NMR to solid tungsten compounds may hold great promise, we have undertaken a 183W MASS NMR investigation of several model compounds and report in this paper the observation of the 183W resonance signals of a variety of such systems. These include several alkali metal and alkaline-earth metal tungstates studied, as in Figure 1A, indicating different chemical environments at the center of the cage. On the other hand, the 183W MASS NMR spectrum of the "Keggin" compound, H3[Ps(WO4)3]·nH2O, in Figure 1B, as expected from its highly symmetric environment.

In Figure 1C, we illustrate the 183W MASS NMR spectrum of WO3, which clearly shows two well-resolved signals, with associated spinning sidebands. The observation of two centerbands in agreement with published X-ray diffraction data, which indicates that there exist two equally abundant, crystallographically distinct WO3 octahedra per unit cell. Finally, in Figure 1D, we illustrate the 183W MASS NMR spectrum of the "Keggin" compound, H3[Ps(WO4)3]·nH2O. In this material there are 12 equivalent W atoms, each octahedrally coordinated by oxygen atoms, forming a cage with the phosphorus site at its center. Phosphorus-31 MASS NMR reveals a single resonance, at δ = −15.1 ppm relative to an aqueous 8S% H3PO4 solution, with a small chemical shift anisotropy, consistent with its symmetric environment at the center of the cage. On the other hand, the 183W MASS NMR spectrum shows a single center peak, with intense spinning sidebands. The chemical shift tensor elements are δ1 = 409, δ2 = 148, and δ3 = −1079 from a saturated Na2WO4 solution (calculated using the Herzfeld–Berger method).

The 183W isotopic chemical shifts of all 10 compounds for which NMR signals have been observed are listed in Table I. Overall, the results we have obtained to date show that in favorable cases it is relatively straightforward, if somewhat time consuming, to obtain solid-state 183W MASS NMR spectra of tungsten-containing compounds. Further studies may reveal whether or not the chemical shift range of WO3 and WO4 structural environments are well separated, as are those of the AlO4 and AlO6 subunits in 7A1 NMR. Since no special instrumentation is required (other than a high-field MASS instrument), it would appear that 183W MASS NMR may become a useful tool for investigating polyoxoanion structure, in investigating the structures of amorphous materials produced by heteropolyanion calculation.

**Table I. Isotopic Chemical Shifts of Some Solid Tungsten Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Iso Shift</th>
<th>Comp Shift</th>
<th>Iso Shift</th>
<th>Comp Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2WO5</td>
<td>515 ppm</td>
<td>515 ppm</td>
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<tr>
<td>Cs2WO4</td>
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<tr>
<td>BaWO4</td>
<td>515 ppm</td>
<td>515 ppm</td>
<td>515 ppm</td>
<td>515 ppm</td>
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</tbody>
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*School of Chemical Sciences.
1Department of Geology.

Figure 1. 183W MASS NMR at 15 MHz (8.45 T); (A) CaWO3, 2.6 kHz MASS, 639 scans, 100 s recycle time, 35 Hz line broadening, 5 µs (89° flip angle); (B) W(CO)5, 2.6 kHz MASS, 416 scans, 200 s recycle time, 1 Hz line broadening, 7 µs (19° flip angle); (C) WO3, 2.8 kHz MASS, 1280 scans, 20 s recycle time, 50 Hz line broadening, 12 µs (33° flip angle); (D) H3[Ps(WO4)3]·nH2O, 2.4 kHz MASS, 3144 scans, 50 s recycle, 30 Hz line broadening, 7 µs (25°) pulse.

*Commercially available compounds used without further purification.
†References to an external saturated aqueous solution of Na2WO4, high-frequency shifts denoted as positive. Errors are ±2 ppm.

or pyrolysis, and in investigating the structures of potential alkanol dehydration catalysts.

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Unusually Basic, Rapidly Protonated Bicyclic Triamine: 11-Methylene-1,5,9-triazabicyclo[7.3.3]pentadecane

Thomas W. Bell,* Heung-Jin Choi, and William Harte

Department of Chemistry, State University of New York Stony Brook, New York 11794-3400

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Macrocyclic polyamines have proven to be useful cation receptors in which multiple pairs of nonbonded electrons stabilize a potent proton receptor in which an exposed basic site provides a charged g~est.l-5 The high basicity of 1,5,9-triazacyclododecane (1) suggests that when three nitrogen atoms are linked in pairs by three-atom bridges the monocation may be stabilized by a hydrogen bonding network, as shown in 1-H+. Nitrogen lone pairs are even more rigidly organized in diazabicyclo[2.3.2]alkanes for which n > 4. For example, Alder et al. have shown that in 1,8-diazabicyclo[6.3.3]tetradecane (2) the internally protonated species is very stable, but it forms extremely slowly by an intramolecular redox process, apparently because the protonation site is shielded from external attack.7 In this paper we describe a combination of the structural features of 1 and 2 that leads to a potent proton receptor in which an exposed basic site provides a pathway for rapid protonation.

The target system of this study, triamine 3, contains a 2-methylene-1,3-propanediyl bridge, which serves as an easily introduced conformational marker and as a potential site for further functionalization. Thus, 1,5,9-triazacyclododecanes and 3-iodo-2-(iodomethyl)-1-propane were added simultaneously to K2CO3 in isopropyl alcohol (Figure 1). The high basicity and lipophilicity of the product became apparent when the pH of the reaction mixture was adjusted to 10–11 by using aqueous NaOH and chloroform was used to extract the product. Hydroiodic acid was sequestered from this basic, iodide-containing solution, for re-crystallization of the chloroform extract afforded 83% of pure 3-HI10 as colorless prisms, mp 199–200 °C. Deprotonation may be accomplished by repeatedly washing a chloroform solution of 3-HI with 2 N aqueous NaOH or by distillation of the salt from powdered KOH. For comparison purposes, the N-methyl derivative 410 was prepared by Eschweiler–Clarke methylation of 3.

Single-crystal X-ray diffraction11 and solution NMR studies of 3-HI confirm the presence of an internal hydrogen bonded network. In the crystal conformation of 3-HI, the smaller bridges are oriented anti to the large bridge, which adopts a chairlike conformation. One N–H proton was located in an "axial" orientation, whereas the internal proton could not be located by difference Fourier maps. The nitrogen atoms form an approximate equilateral triangle with an average interatomic distance of 2.75 Å. The internal proton, which was fixed at a bridgehead nitrogen for calculation purposes, probably exchanges rapidly between the three sites. Proton NMR spectroscopy,12 in combination with various two-dimensional NMR methods (COSY, CSCM, and NOESY), indicates that 3-HI adopts a very similar conformation in CDCl3 solution. As expected from the crystal conformation of 3-HI, the exocyclic methylene protons (H, δ 5.00) are significantly coupled only to the out-of-plane allylic protons (Hb, δ 3.90, J = 1.7 Hz). Their geminal partners (Hb', δ 3.05, J = 13.5 Hz) are expectedly shielded by the anti-directed bridgehead lone-pair electrons.13 A significant 2D NOE correlation is observed between Hb and Hc (Figure 2).

(6) pKb = 13.2, pKc = 7.45, pKd = 12.6, pKg = 7.6.19
(11) Space group P21. Unit cell parameters: a = 13.487 (3) Å, b = 8.909 (2) Å, c = 13.797 (5) Å, β = 111.62°. V = 1541 (1) Å3. Densities: Dc = 1.514 g/cm3, Dm = 1.476 g/cm3. Formulas: C20H26N3I (351.28 amu). Intermolecular density was measured on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) in the w = 2θ mode. The structure was solved by the Patterson method using 659 of the 1514 reflections measured. Most hydrogen atom positions were calculated using standard geometries in the later stages of refinement. Refinement factors: R1 = 0.057, R2 = 0.062. Bond angles and lengths and positional and thermal parameters are included as supplementary material. (b) At 100 MHz in CDCl3 (20 °C) the NH protons of 3-HI are both deshielded (10.5 and 11.5 ppm), indicating that the large bridge may undergo rapid inversion. At 40 °C these resonances are coalesced.