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Solid-State Tungsten-183 Nuclear Magnetic Resonance Spectroscopy

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We report the first direct observation of the ^{183}W 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 ^{183}W NMR has been clearly demonstrated in solution,[1] as, for example, in determining the structures of isopolytungstates, or "Keggin" cluster compounds,[2-4] the successful application of high-resolution ^{183}W MASS NMR to solid compounds has not been reported.[5] This is at first sight surprising in view of the moderately favorable magnetic properties of the ^{183}W nucleus[6] ($I = {}^1/_2$, abundance = 14.4%, Ξ = 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 ^{183}W MASS NMR investigation of several "model" compounds and report in this paper the observation of the ^{183}W resonance signals of a variety of such systems. These include several alkali metal and alkaline-earth metal tungstates (M_2WO_4, where M = Li, Na, K, and Cs, and MWO_4, where M = Ca, Sr, and Ba), tungsten hexacarbonyl, tungsten trioxide, and the "Keggin" compound phosphotungstic acid, $H_3[P(W_{12}O_{40})]\cdot nH_2O$.

In Figure 1 we show the ^{183}W MASS NMR spectra of some of the model tungsten compounds recorded at 8.45 T (15 MHz), chemical shifts being referenced to the ^{183}W NMR signal of an external saturated solution of Na_2WO_4, high frequency shifts being denoted positive. Preliminary observations indicate that the ^{183}W nucleus displays long spin–lattice relaxation times in all cases investigated, an observation that helps to account for the relatively low signal-to-noise ratio of the spectra. Figure 1A–D shows the ^{183}W MASS NMR spectra of $CaWO_4$ (scheelite), WO_3, $W(CO)_6$, and $H_3[P(W_{12}O_{40})]\cdot nH_2O$. A single, sharp resonance with no spinning sidebands is observed for all the alkali metal and alkaline-earth metal tungstates studied, as in Figure 1A, indicating a small chemical shift anisotropy and confirming the symmetric environment of the tungsten site predicted by X-ray and/or neutron diffraction studies of these compounds.[7] A very sharp signal (FWHH = 6 Hz), again with no spinning sidebands, is also seen for $W(CO)_6$ (Figure 1B), as expected from its highly symmetric environment.[8] Figure 1C illustrates the ^{183}W MASS NMR spectrum of WO_3, which clearly shows two well-resolved signals, with associated spinning sidebands. The observation of two centerbands is in agreement with published X-ray diffraction data,[9] which indicates that there exist two equally abundant, crystallographically distinct WO_6 octahedra per unit cell. Finally, in Figure 1D, we illustrate the ^{183}W MASS NMR spectrum of the "Keggin" compound, $H_3[P(W_{12}O_{40})]\cdot nH_2O$. 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.[10] Phosphorus-31 MASS NMR reveals a single resonance,[11] at δ −15.1 relative to an aqueous 85% H_3PO_4 solution, with a small chemical shift anisotropy, consistent with its symmetric environment at the center of the cage. On the other hand, the ^{183}W MASS NMR spectrum shows a single center peak, with intense spinning sidebands. The chemical shift tensor elements are δ_{11} 409, δ_{22} 148, and δ_{33} −1079 from a saturated Na_2WO_4 solution (calculated using the Herzfeld–Berger method).[12]

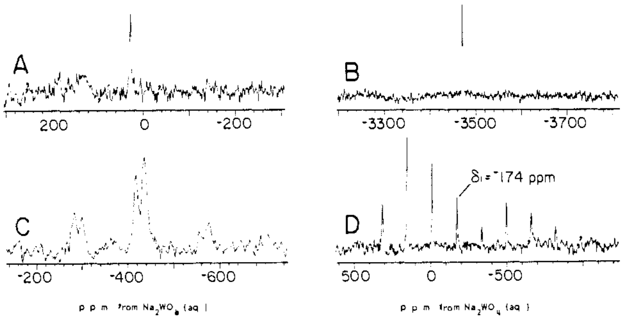

Figure 1. ^{183}W MASS NMR at 15 MHz (8.45 T): (A) $CaWO_4$, 2.6 kHz MASS, 639 scans, 100 s recycle time, 35 Hz line broadening, 5 μs pulse (18° flip angle); (B) $W(CO)_6$, 2.6 kHz MASS, 416 scans, 200 s recycle time, 1 Hz line broadening, 7 μs pulse (19° flip angle); (C) WO_3, 2.8 kHz MASS, 1280 scans, 20 s recycle time, 50 Hz line broadening, 12 μs pulse (33° flip angle); (D) $H_3[P(W_{12}O_{40})]\cdot nH_2O$, 2.4 kHz MASS, 3114 scans, 50 s recycle, 30 Hz line broadening, 7 μs (25°) pulse.

Table I. Isotropic Chemical Shifts of Some Solid Tungsten Compounds

compd[a]	chem shift $\delta_i^{b,c}$ (ppm)	compd[a]	chem shift $\delta_i^{b,c}$ (ppm)
Li_2WO_4	−40	$SrWO_4$	−33
Na_2WO_4	−63	$BaWO_4$	−78
K_2WO_4	−18	WO_3	−414, −438
Cs_2WO_4	−36	$W(CO)_6$	−3470
$CaWO_4$ (scheelite)	29	$H_3[P(W_{12}O_{40})]\cdot nH_2O$	−174

[a] Commercially available compounds used without further purification. [b] Referenced to an external saturated aqueous solution of Na_2WO_4, high-frequency shifts denoted as positive. [c] Errors are ±2 ppm.

The ^{183}W isotropic 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 ^{183}W MASS NMR spectra of tungsten-containing compounds. Further studies may reveal whether or not the chemical shift ranges of WO_4 and WO_6 structural environments are well separated, as are those of the AlO_4 and AlO_6 subunits in ^{27}Al NMR.[13] Since no special instrumentation is required (other than a high-field MASS instrument), it would appear that ^{183}W MASS NMR may become a useful tool for investigating polyoxoanion structure, in investigating the structures of amorphous materials produced by heteropolyanion calcination

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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

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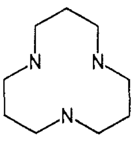
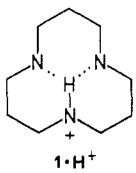
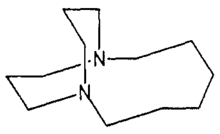
Macrocyclic polyamines have proven to be useful cation receptors in which multiple pairs of nonbonded electrons stabilize a charged guest.[1-5] The high basicity of 1,5,9-triazacyclododecane (**1**)[6] suggests that when three nitrogen atoms are linked in pairs by three-atom bridges the monocation may be stabilized by a hydrogen bonding network, as shown in **1**·H$^+$. Nitrogen lone pairs are even more rigidly organized in diazabicyclo[*n*.3.3]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.



1



1·H$^+$



2

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-triazacyclododecane[8] and 3-iodo-2-(iodomethyl)-1-propene[9] were added simultaneously to K_2CO_3 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. Hydriodic acid was sequestered from this basic, iodide-containing solution, for recrystallization of the chloroform extract afforded 83% of pure **3**·HI[10] 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 **4**[10] was prepared by Eschweiler–Clarke methylation of **3**.[10]

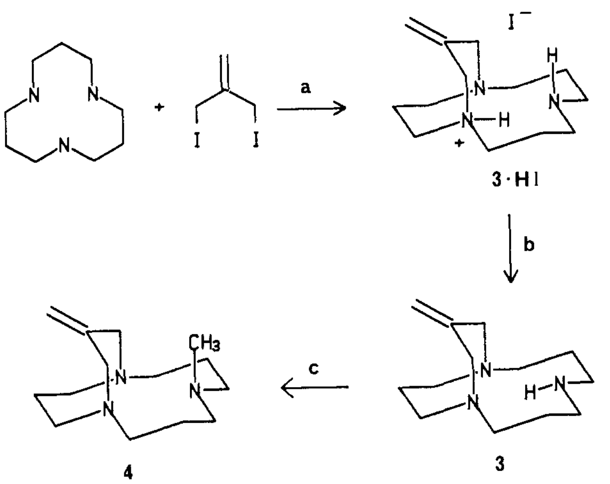


Figure 1. Synthesis of 11-methylene-1,5,9-triazabicyclo[7.3.3.]pentadecane (**3**) and *N*-methyl derivative **4**: (a) K_2CO_3, isopropyl alcohol, reflux (83%); (b) KOH, distillation at 110 °C, 1 mmHg (74% overall); (c) HCO_2H, CH_2O, H_2O, 120 °C, 6 h; distillation at 100–110 °C, 0.3 mmHg (60%).

Single-crystal X-ray diffraction[11] 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 $CDCl_3$ solution. As expected from the crystal conformation of **3**·HI, the exocyclic methylene protons (H_a, δ 5.00) are significantly coupled only to the out-of-plane allylic protons (H_b, δ 3.90, $J_{ab} = 1.7$ Hz). Their geminal partners (H_b', δ 3.05, $J_{bb'} = 13.5$ Hz) are expectedly shielded by the anti-directed bridgehead lone-pair electrons.[13] A significant 2D NOE correlation is observed between H_a and H_c (Figure 2).

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(6) pK_{a_3} = 13.2, pK_{a_2} = 7.4;[4] pK_{a_3} = 12.6, pK_{a_2} = 7.6.[5b]

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(10) All new compounds gave ^1H NMR, ^{13}C NMR, IR, and microanalytical data (C, H, N: ±0.3%) consistent with the proposed structures.

(11) Space group *Cc*. Unit cell parameters: $a = 13.487$ (3) Å, $b = 8.909$ (2) Å, $c = 13.797$ (5) Å, $\beta = 111.62°$, $V = 1541$ (1) Å^3, $Z = 4$. Densities: $D_c = 1.514$ g/cm^3, $D_m = 1.476$ g/cm^3. Formula: $C_{13}H_{26}N_3I$ (351.28 amu). Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) in the $\omega - 2\theta$ 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: $R_{uw} = 0.057$; $R_w' = 0.062$. Bond angles and lengths and positional and thermal parameters are included as supplementary material.

(12) At 300 MHz in $CDCl_3$ (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.

(13) Similar shielding effects are observed for protons α to nitrogen in six-membered rings. For example, see: Overman, L. E.; Bell, K. L.; Ito, F. *J. Am. Chem. Soc.* **1984**, *106*, 4192–4201. Weisman, G. R.; Johnson, V.; Fiala, R. E. *Tetrahedron Lett.* **1980**, *21*, 3635–3638 and references therein.

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