polymer. The rotation about the molecular axis is severely restricted in the glassy state, where only solid-state-type rotational jumps by 180° are observed. This behavior is not unique to the systems studied here, e.g., the analogous liquid crystalline polymer with a spacer length of $m = 2$ (Figure 1) shows[23] a similar restricted motion below T_g. Rotational jumps of phenyl rings by 180° have also been proposed to exist in low molecular weight liquid crystalline systems and have recently been observed, e.g., for side groups in the crystalline pentapeptide enkephalin[30] and amorphous polystyrene[31] below T_g.

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Registry No. Deuterated acrylate monomer ($n = 2$), 80434-50-0; deuterated acrylate monomer ($n = 6$), 80434-51-1; deuterated acrylate polymer ($n = 2$), 80434-75-9; deuterated acrylate polymer ($n = 6$), 80434-76-0.

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High-Resolution NMR Spectroscopy of Quadrupolar Nuclei in Solids: Sodium Salts

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Most elements that have a nuclear spin are quadrupolar, and it is generally accepted that high-resolution solid-state NMR studies of these systems using magic-angle sample spinning will be very difficult for nuclei having quadrupole coupling constants $\gtrsim$100 kHz, due to technical limitations on rotor stability, and the presence of second-order quadrupolar broadening.[1-5] This view is of course correct for integral spins $I = 1, 2, 3$, etc., but about two out of three elements that possess nuclear spin have nonintegral spins $I = {}^3/_2, {}^5/_2, {}^7/_2$, or ${}^9/_2$. The central $({}^1/_2, -{}^1/_2)$ spin transition is only broadened by dipolar, chemical shift (or Knight shift) anisotropy and *second-order* quadrupolar broadening, and thus these $({}^1/_2, -{}^1/_2)$ line widths are generally $\ll e^2qQ/h$. We show in this communication that high-resolution solid-state spectra may be easily obtained for ^{23}Na nuclei having e^2qQ/h values of up to 2–3 MHz, by monitoring the $({}^1/_2, -{}^1/_2)$ spin transition selectively under conditions of rapid sample rotation, and note that these values may be increased to ~10–15 MHz for other nuclei at higher magnetic field strengths, using high-field high-speed sample spinning techniques.

We show in Figure 1 ^{23}Na Fourier transform NMR spectra of a variety of ^{23}Na-containing solids, in which e^2qQ/h values vary from ~0 to ~2.6 MHz.[6-10] Figure 1A shows static and magic-angle spinning spectra of ^{23}NaCl, a cubic structure having $e^2qQ/h \sim 0$. As reported previously by others[1,10] there is considerable line narrowing upon rotation at a rate of ~2 kHz, the static breadth. Similar results are, however, also obtained when investigating ^{23}NaBrO$_3$ (Figure 1B) where e^2qQ/h values of 0.864 (±0.008) MHz with $\eta \sim 0$ have been reported previously.[8,9] The explanation, as suggested above, is that we are observing only the $({}^1/_2, -{}^1/_2)$ spin transition and that the second-order broadening in this system is small (1–2 kHz[11,12]) and, moreover, is substantially averaged upon magic-angle rotation, as seen more clearly below. Partial averaging of second-order quadrupolar broadening by spinning at 90° to the applied field has been noted previously by Nolle[13] in which Mo(CO)$_6$ ($e^2qQ/h \sim 21$ kHz, $W_{1/2}^{(2)} \lesssim 100$ Hz) was rotated at speeds of up to 80 Hz[13] and was first investigated theoretically by Andrew.[14]

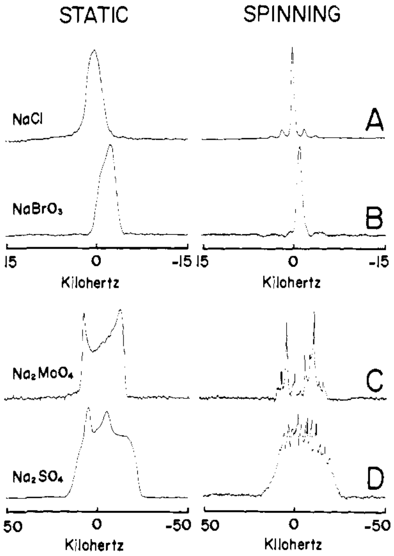

Figure 1. 40-MHz ^{23}Na Fourier transform NMR spectra of various ^{23}Na salts, with and without magic-angle ($\theta = 54.7°$) sample spinning. (A) NaCl ($e^2qQ/h \sim 0$); (B) NaBrO$_3$ ($e^2qQ/h \sim 860$ kHz, $\eta \sim 0$); (C) Na$_2$MoO$_4$ (anhydrous, $e^2qQ/h \sim 2.6$ MHz, $\eta \sim 0$); (D) Na$_2$SO$_4$ ($e^2qQ/h \sim 2.6$ MHz, $\eta \sim 0.6$). Samples were spun at ~2–3 kHz; sample size was ~0.5 cm^3. The number of scans varied but was typically in the range 100–200. Chemicals were reagent grade and were checked by microanalysis. Spectra were recorded on a home-built instrument operating with a 3.5-T, 4.0-in. bore, superconducting solenoid.

For larger values of e^2qQ/h, for example, in the cubic spinel ^{23}Na$_2$MoO$_4$ ($e^2qQ/h \sim 2.6$ MHz, $\eta = 0 \pm 0.1$ ref 6) or in ^{23}Na$_2$SO$_4$ ($e^2qQ/h \sim 2.6$ MHz, $\eta \sim 0.6 \pm 0.1$, ref 7), residual second-order breadths are much larger, since the broadening is $\propto (e^2qQ/h)^2$. Residual breadths of ≈20–30 kHz are thus observed (at 3.5 T), with the result that numerous spinning sidebands or rotational echoes are obtained in the spinning experiment[15,16] (Figure 1C,D).

The results of Figure 1C,D indicate the need for (a) much higher field operation and (b) much higher spinning speeds, if such spinning experiments are to be of general utility, since the second-order broadenings are $\propto H_0^{-1}$. In addition, we have found that, as expected,[3,17] magic angles other than 54.7° are more

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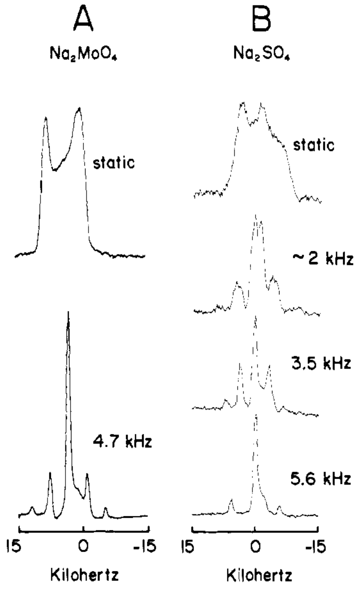

Figure 2. 95-MHz ^{23}Na Fourier transform NMR spectra of Na_2MoO_4 and Na_2SO_4. (A) Na_2MoO_4, static and spinning at 4.7 kHz and $\theta = 38°$; (B) Na_2SO_4, static and spinning at $\theta = 48°$ at the speeds indicated. Spectra were recorded on a home-built instrument operating with an 8.5-T, 3.0-in. bore, superconducting solenoid.

effective in reducing second-order quadrupole interactions. We show therefore in Figure 2A,B spectra of $^{23}Na_2MoO_4$ and $^{23}Na_2SO_4$ at 8.5 T (corresponding to a ^{23}Na resonance frequency of 95.2 MHz) for spinning speeds up to ~6 kHz. For the static samples, the line widths are reduced to ≈10-12 kHz upon increasing H_0 from 3.5 to 8.5 T. At low spinning speeds there are again spinning side bands, but for fast (≳3 kHz) rotation well-resolved center bands are obtained (Figure 2A,B) for both Na_2MoO_4 ($\eta = 0$) spinning at $\theta = 38°$ and for Na_2SO_4 ($\eta = 0.6$) spinning at $\theta = 48°$, although the lines are still asymmetric, and for the general case of an unknown e^2qQ/h, appropriate corrections to the observed shift cannot readily be made. These will, however, be of the order of the line width for e^2qQ/h of ~1-3 MHz and may be determined from frequency dependence studies. These results, together with those we have obtained on a variety of other nuclei having spins $I = {}^3/_2, {}^5/_2, {}^7/_2$, and ${}^9/_2$ (e.g., ^{11}B, ^{27}Al, ^{51}V, ^{55}Mn, and ^{93}Nb),[12,18] including the observation of fine structure in one system having $e^2qQ/h = 19.5$ MHz,[12] together with recent independent work on ^{27}Al by Muller et al.[19] and on ^{23}Na by Kundla et al.[20] using magic-angle (54.7°) spinning, strongly suggest that it is now possible to investigate a greatly increased number of nuclei in the periodic table in solid-state systems of chemical and biological interest. For high-resolution studies, the results of Figures 1 and 2 clearly indicate the need of operating at the highest field strengths possible (≥12 T) together with the need for development of ultra-high-speed variable-angle spinner assemblies; studies of a variety of organometallics (^{55}Mn, ^{95}Mo, ^{99}Ru), borates and boron hydrides (^{11}B), oxides (^{17}O), supported catalysts and zeolites (^{27}Al), and metalloprotein model systems (^{63}Cu, ^{67}Zn) are currently in progress.

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Registry No. NaCl, 7647-14-5; $NaBrO_3$, 7789-38-0; Na_2MoO_4, 7631-95-0; Na_2SO_4, 15124-09-1.

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Pyrazolyl-Bridged Iridium Dimers. 1. Accommodation of Both Weak and Strong Metal-Metal Interactions by a Bridging Pyrazolyl Framework in Dissymmetric Dimeric Structures

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The chemistry of polynuclear transition-metal compounds has entered a phase of extremely rapid development, as a consequence of progressive rationalization of synthetic stragety as well as increased access to appropriate characterization techniques. This activity reflects a high level of interest in the influence of one another of neighboring metal centers, electronically in terms of excited-state phenomena[1] or electron delocalization between adjacent atoms[2] or chemically in relation to reactivity at (especially multiple) metal-metal bonds[3] and cooperative catalytic action, including efforts to substantiate a "cluster/surface" analogy.[4] Such effects will be manifested in their simplest form in dimeric complexes, principles established from which may be ultimately translated into the context of larger aggregates of metal atoms. We have commented recently[5] on the versatility of the η^2-pyrazolyl group as a bridging ligand, which can straddle an unusually wide range of intermetallic separations to hold two adjacent metal centers in a chemically extremely stable configuration. Here we show that the same linkage can absorb drastic contraction of a bridged framework, arising through metal-metal bond formation accompanying oxidation at each atom in a dimeric array. This has been identified during a systematic investigation of the structure and reactivity of a series of pyrazolyl-bridged iridium(I) complexes, a novel class of bimetallics, the chemistry of which combines a number of remarkable features.

Reaction between *trans*-Ir$(PPh_3)_2$(CO)(Cl) (Vaska's complex) and pyrazolide anion (ambient, THF, 6 h) affords blood-red crystals of dicarbonylbis(triphenylphosphine)di-μ-pyrazolyl-diiridium(I) (**1**) (30-60%), characterized by[6] single-crystal X-ray diffractometry (Figure 1). The same compound can be synthesized stepwise from $[(COD)IrCl]_2$ (COD = 1,5-cyclo-

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