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SOLID-STATE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL COORDINATION COMPLEXES AND ORGANOMETALLICS

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CONTENTS

A. HISTORICAL

Nuclear magnetic resonance spectroscopy is a powerful tool for the characterization of chemical species. Although the first spectra were obtained with solid samples (proton in paraffin), most NMR studies have been carried out in the liquid phase, namely in solution. This may be due to the large amount of chemical information which can be derived from high-resolution NMR spectroscopy.

The improvement of the pulse technique and other instrumental developments have made it possible to extend these detailed studies to solid samples (crystalline and amorphous), gels and surface-adsorbed species. The cross-polarization/magic angle spinning (CP/MAS) techniques were elucidated in the early 1970s, and spectrometers which have CP/MAS attachments as well as other newer NMR spectroscopies such as COSY, 2D-NMR, and WEFT, have become much more familiar in the recent decade.

Pioneering work was carried out by Andrew [1–4] in the 1950s using magic angle spinning, and demonstrating the differences between the two sites of phosphorus in phosphorus pentachloride [3,4], namely $[PCl_4]^+[PCl_6]^-$. Recent improvements in NMR facilities, such as superconducting magnets and the application of fast Fourier-transform algorithms, have caused a rapid growth in the literature of this interesting research area since 1980. This powerful spectroscopy is an important tool for studying the characteristics of many chemical species in the solid state, mostly in coordination and organometallic chemistry. There are many coordination species which are only stable in the solid phase, or rapid exchange in solution can prevent the observation of a desired species in solution.

The increasing number of reports dealing with CP/MAS NMR spectroscopy as recorded by *Chemical Abstracts* is shown in Fig. 1 plotted against the year. The figures are also given in Table 1. Most CP/MAS spectroscopy papers are in the area of macromolecules, fossil fuels, and aluminosilicate mineralogy (mainly zeolites). In these areas, there are many excellent reviews by pioneering researchers. Moreover, several monographs have been published. Therefore, we will summarize here only magic angle NMR spectroscopy research in coordination chemistry and organometallics.

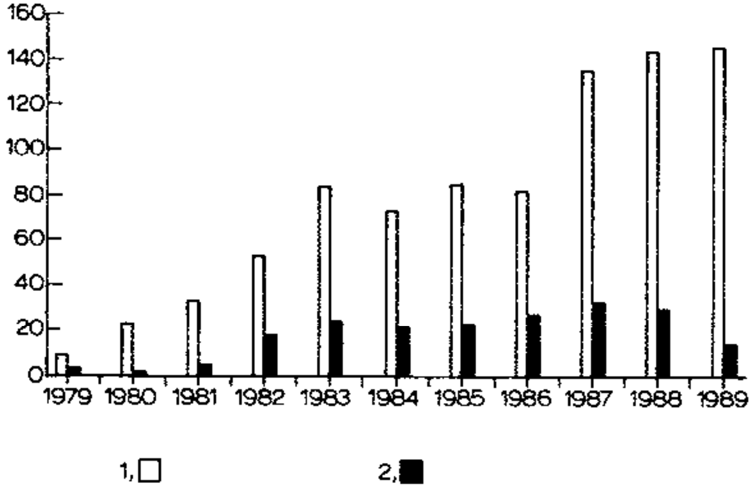

Fig. 1. Increasing trend of CP/MAS NMR papers. 1, CP/MAS NMR papers from *Chemical Abstracts* (all). 2, Coordination and organometallic chemistry CP/MAS NMR papers. Although there are some time lags between the original publication and its citation in *Chemical Abstracts*, this shows the remarkable increase in the number of papers for this relatively unique area.

TABLE 1

Annual change of CP/MAS literature for coordination and organometallic complexes

Year	*Chem. Abstr.* Vol. no.	CP/MAS in		Refs.
		Chem. Abstr.	Coord. and organomet.	
1979	90/91	9	3	15, 16
1980	92/93	23	1	17
1981	94/95	33	6	18–23
1982	96/97	53	18	5, 24–39
1983	98/99	84	24	6–8, 40–60
1984	100/101	73	22	9, 61–81
1985	102/103	85	23	82–103
1986	104/105	82	28	10, 104–130
1987	106/107	135	33	131–163
1988	108/109	144	30	11–14, 164–189
1989	110/111	146	14	190–203
		Total	202	

B. THE NMR SPECTRAL SHAPE OF POLYCRYSTALLINE SOLID SAMPLES

(i) Spin Hamiltonians

The typical spin Hamiltonian which describes the resonance conditions of magnetic nuclei can be expressed as the sum of four terms, namely H_{CS} (chemical shift), H_J (spin–spin coupling), H_D (dipolar), H_Q (quadrupolar).

$$H = H_{CS} + H_J + H_D + H_Q$$

The last two terms are usually averaged to zero in the liquid samples because of the rapid random motions, but they play a dominant role in the solid state samples. These contributions are hundreds or several thousand times larger than H_{CS}. These differences cause the broad and almost featureless solid-phase NMR spectra, and the earlier studies were therefore limited only to wide-line NMR spectroscopy (mainly proton NMR). Of course the spectral characteristics of quadrupolar nuclei are usually largely affected by the electric field gradient at their sites, both in the liquid and solid phases.

(ii) Magic angle spinning

The dipolar term contains the angular-dependent term which is proportional to $(1-3\cos^2\theta)$, where θ is the angle between the dipole vector and the magnetic field axis. The rapid molecular tumbling in the liquid phase averages this contribution to almost zero. In the polycrystalline solid phase, there exist many different definite angles in the sample specimen. Therefore, the resonant line clearly reveals the chemical shift anisotropy. The three components σ_{11}, σ_{22} and σ_{33} can be derived from typical polycrystalline solid state samples. If the chemical shift tensors have axial symmetry, spectral lines can be simplified and only two σ ($\sigma_{\parallel}$ (parallel) and $\sigma_{\perp}$ (perpendicular)) can be obtained (see Fig. 2).

When the axis of a sample is exactly inclined at 54.7° ($= \cos^{-1}(1/\sqrt{3})$) from the direction of magnetic field, one may eliminate the dipolar contributions if the spinning frequency is much larger than the anisotropic chemical shift difference frequency ($\Delta\sigma$). This angle is usually called the 'magic angle'. Therefore, high-resolution NMR spectroscopy for solid samples is usually called 'MAS' (or MAR) NMR.

Many half-spin nuclei, which are not affected by quadrupolar relaxation, can show relatively sharp spectra, revealing the characteristics of the molecular moiety in the solid phase, if this dipolar contribution can be eliminated efficiently.

In the central metal nuclei of the heavier elements, chemical shift anisotropy is sufficiently large that, given the mechanical limits to rotating samples at high speed rates, one can not efficiently erase the side bands. For instance, platinum-195 in potassium tetrachloroplatinate(II) shows an anisotropic chemical shift of about 1% (= 10 000 ppm) [117,130]. This is hardly erasable

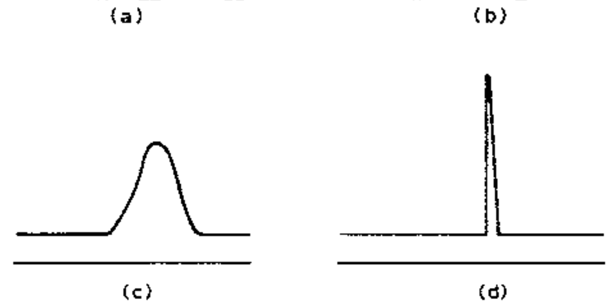

Fig. 2. NMR lineshape of polycrystalline solid samples. (a) Anisotropic, three chemical shift values; (b) axially symmetric, two chemical shift values; (c) insufficient averaging by slow sample rotation; (d) sharp signal by sufficient averaging by rapid rotation.

by the ordinary magic angle spinning frequency (3–4 kHz), if the measurements are carried out in a superconducting magnet spectrometer.

C. CROSS-POLARIZATION

The magnitudes of the NMR signals of the less-abundant nuclei such as carbon-13 (natural abundance 1.108%) and nitrogen-15 (0.37%) are usually extremely poor and several techniques have been introduced to enhance them. One of the most powerful techniques is to enrich the magnetic nuclei in these samples, but this is not always possible. The longitudinal relaxation time (T_1) of the nuclei in the solid diamagnetic samples is usually too long, and not appropriate for NMR measurements. The nuclei of longer relaxation times could show sharp spectra, but their easy saturation causes a decrease of signal intensity. Even if pulse FT techniques are applied, the long relaxation time needs long pulse intervals, and a decrease in the number of integrations.

Special multipulse proton decoupling sequences enable one to shorten the relaxation time of the less-abundant nuclei such as carbon-13. This technique is usually called 'polarization transfer'. The carbon spin which absorbs the electromagnetic radiation is thermodynamically 'hot', and the protons which connect with carbons act as the 'cold' reservoir. The energy transitions from carbon spin and protons become rapid, and the T_1 of carbon-13 is effectively shortened. The contribution of the dipolar term is very important in the solid phase, and this improves the signals even if there is no chemical bonding. This 'cross-polarization' makes it possible to shorten the pulse interval, and increase dramatically the pulse repetition.

One interesting example is xenon-129 NMR in the inclusion compounds, reported by Ripmeester [37,180]. The existence of a 'physical shift' with xenon-129 had already been shown in 1966, but the differences in the gyromagnetic ratios in various inclusion compounds such as β-quinol and phenol clathrates provide much information to characterize the state of this noble gas atom. Although there is no direct chemical bonding between xenon and the protons in the host lattice, cross-polarization increases the sensitivity, providing useful additional information.

D. CARBON-13 NMR

Most CP/MAS NMR studies in coordination chemistry involve carbon-13 since metal coordination complexes and organometallic compounds usually contain many carbon atoms in the ligand skeleton. The carbon-13 spectra for these ligand skeletal carbon atoms reveal the small differences in magnetic environment in the solid state.

Freshly recrystallized lead diacetate shows very simple carbon-13 spectra which are much different from the aged and commercial product [62]. The last two showed the existence of many different sites corresponding to different environments of the acetate groups in the crystal. This demonstrates an interesting application to characterize precisely the solid state structure in such simple salts.

The stereochemical sites of the ligand skeleton, such as differences in conformation, can be clearly observed with CP/MAS spectroscopy. For instance, with K[Co(edta)] four different carboxyl carbon sites can be identified with the carbon-13 CP/MAS NMR. The rapid conformational change in the solution state can be frozen in the solid state [204].

The scalar coupling constants between tin-119 and carbon-13 were observed in the solid state in several methyltin compounds. A linear relationship was clearly demonstrated between these coupling constants and Me–Sn–Me angles for 10 compounds [91]. In many organometallic compounds, carbonyl carbon atoms, which have no directly coupled protons, are usually not so easy to detect because of the lack of nuclear Overhauser effect (NOE) enhancement and cross-polarization. Isotopic enrichment was effective for these samples which contain no protons.

The longer relaxation times of carbon-13 are effectively shortened by the introduction of high-power decoupling and the cross-polarization technique. Even if there are no directly coupled protons, the dipolar decoupling can be effective when protons exist at geometrically neighbouring sites. This dipolar decoupling is only effective in the short-range since it is inversely proportional to the cube of the radius.

The temperature dependence of the spectral change can show the presence of fluxional behaviour in the solid phase. Tri-iron dodecacarbonyl [18,30,116] showed a characteristic spectral change in the carbon-13 CP/MAS spectra. These dynamic NMR studies can give many useful results if the MAS NMR can be measured over a wide temperature range.

E. OTHER HALF-SPIN NUCLEI IN LIGANDS

Because of the narrow chemical shift range, proton MAS NMR has rarely been studied until now. Protons have been characterized in crystals (hydrated water, zeolitic water or hydroxyl protons), and in several hydrated minerals or intercalate compounds [57,168]. This can be useful if applied to other inorganic solids containing oxo groups or two hydroxyl groups which are poorly characterized by X-ray crystallography.

Other than carbon-13, the most intensively studied nuclei in this case are phosphorus-31 and silicon-29. Favourable cases include phosphorus-31 in phosphine and phosphite complexes, and nitrogen-15 in ammine complexes. The relaxation times of these ligand nuclei in the solid phase are usually long, and spectral measurements are not so facile without polarization transfer. If there is strong coupling with protons, the measurements do become much easier than for carbon-13 because of their higher sensitivities and natural abundances.

Triphenylphosphine complexes with univalent Group 11 metal salts (Cu, Ag, Au) were extensively studied by phosphorus-31 CP/MAS NMR by Australian groups [106,134,135]. These complexes are relatively labile in solution, and their independent characterization by phosphorus-31 NMR clearly reveals the slight differences in these analogous complexes. Other phosphine or phosphite species studied by phosphorus-31 CP/MAS NMR included complexes of palladium(II) [26,123,186], platinum(II) [26,27,43,186] and mercury(II) [104]. Large spin–spin coupling can be observed in the last two cases.

The structures of immobilized metal–phosphine complex species on the surfaces of silica gel and glass beads, as well as in the polymer-bound complexes, were also determined well by phosphorus-31 CP/MAS NMR [26,27].

Many polyphosphate anions can be characterized in the crystalline phase by MAS NMR techniques [112,118,128,152]. The in situ characterization of several calcium phosphates in chicken bones [78] showed the effectiveness of this technique in bioinorganic chemistry.

Nitrogen-15 CP/MAS spectroscopy has been studied in only a few cases with the use of isotope labelling. The ^{15}NO nitrosyl complexes of ruthenium(II) were analyzed to determine the molecular geometry, and the differences between the linear M–N–O and bent M–N–O groups are clearly distinguished [96].

It is interesting that the effect of counterions of various ammonium salts [81] can be clearly observed on the chemical shift of nitrogen-15 as well as fluorine-19 in various fluorides [110].

F. CENTRAL METAL NUCLEI

(i) Half-spin nuclei

There have been few MAS NMR studies of half-spin nuclides. They include cadmium-113, tin-119, platinum-195 and mercury-199. Their rarity is due to the large shielding anisotropies in the heavier elements.

Among these, cadmium-113 solid-state NMR has been studied most extensively. The relatively higher sensitivity and medium natural abundance make it possible to widen the number of applications in the future. The chemical shift anisotropy is several hundred ppm in magnitude, easily eliminated by ordinary sample spinning even in superconducting magnets. The biochemically interesting cadmium complexes (cadmium(II) ion easily substitutes sites of calcium(II) or zinc(II)) can provide important bioinorganic information. The excellent review by Summers [14] includes about 30 papers dealing with solid-state cadmium-113 NMR. Most of these papers include only brief descriptions of the solid-state cadmium-113 NMR data (because the main theme of the papers is X-ray crystallography), but there are some interesting characteristics for a variety of complexes [15,16,38,39,46,51,59,63,73,77, 96,100,101,129,130,157].

Tin-119 NMR would also be expected to be easily measured, and there is a greater variety of chemical species available. Organotin complexes such as trimethyltin halides have been studied by high-resolution solid-state NMR spectroscopy [44,52,86,87,88,109]. The shielding anisotropy seems to be almost comparable with that of cadmium-113.

Among the half-spin nuclides of the elements of the 6th period, tungsten-183 [133], mercury-199 [146] and platinum-195 [29,56,131] are the most interesting. Thallium-205 has much better NMR sensitivity, and usually its spectra can be observed even without magic angle spinning. The other half-spin nuclides, such as lead-207 [121,178], have only rarely been studied. The chemical shift anisotropies in the less symmetrical complexes for these heavy nuclides are exceedingly large, and may not be eliminated even with the highest spinning frequency. The air-turbine rotors can be spun at around several kHz, which seems to be the mechanical limit from aerodynamics. Because the chemical shift difference frequency is proportional to the resonant frequency, this upper limit rotation rate determines the limit of resonant condition for these heavier nuclides. Of course these nuclides in a highly symmetric environment show clear solid-state spectra (for example, K_2PtCl_6) showing a much different pattern from the tetragonally distorted K_2PtCl_4 [131].

Tungsten-183 is expected to be useful to characterize many heteropoly anions, but the shielding anisotropy is very large and the suppression of side bands is very difficult for the case of phosphotungstic acid [133]. Simple species such as sodium tungstate or tungsten hexacarbonyl show very sharp lines.

The first data for a scalar coupling constant between tellurium-125 and chlorine-35,37 were observed by CP/MAS NMR spectroscopy [140]. The important nuclides of half-spin are tabulated in Table 2 with gyromagnetic ratios and natural abundances.

The large range of chemical shift and the narrow line widths can provide much detailed information. The applications of this MAS NMR for many different nuclei are expected to expand into various fields of coordination chemistry.

TABLE 2

Half-spin nuclides for MAS NMR

Nucleus	Spin	Natural abundance (%)	Resonant frequency at 2.35 T (MHz)	Q
^{1}H	1/2	99.985	100.000	
^{13}C	1/2	1.108	25.145	
^{15}N	1/2	0.37	7.226	
^{19}F	1/2	100	94.094	
^{29}Si	1/2	4.70	19.867	
^{31}P	1/2	100	40.480	
^{57}Fe	1/2	2.19	3.238	
^{77}Se	1/2	7.58	19.072	
^{89}Y	1/2	100	4.920	
^{103}Rh	1/2	100	3.156	
^{107}Ag	1/2	51.82	4.048	
^{109}Ag	1/2	48.18	4.654	
^{111}Cd	1/2	12.75	21.202	
^{113}Cd	1/2	12.26	22.179	
^{115}Sn	1/2	0.35	32.718	
^{117}Sn	1/2	7.61	35.632	
^{119}Sn	1/2	8.58	37.290	
^{123}Te	1/2	0.87	26.169	
^{125}Te	1/2	7.03	31.591	
^{129}Xe	1/2	32.4	27.856	
^{169}Tm	1/2	100	7.990	
^{171}Yb	1/2	14.31	17.699	
^{183}W	1/2	14.28	4.218	
^{187}Os	1/2	1.64	2.282	
^{195}Pt	1/2	33.8	21.496	
^{199}Hg	1/2	16.84	17.870	
^{203}Tl	1/2	29.50	57.073	
^{205}Tl	1/2	70.50	57.634	
^{207}Pb	1/2	22.6	20.920	
Other important quadrupolar nuclei for MAS NMR				
^{23}Na	3/2	100	26.429	0.10
^{27}Al	5/2	100	26.077	0.14
^{51}V	7/2	99.76	26.350	0.052
^{55}Mn	5/2	100	24.840	0.40
^{59}Co	7/2	100	23.727	0.42
^{63}Cu	3/2	69.09	26.515	−0.22
^{93}Nb	9/2	100	24.549	−0.32
^{133}Cs	7/2	100	13.210	−0.003

(ii) Quadrupolar nuclei

The quadrupolar nuclei show a remarkable line width change because of the existence of electric field gradients. This occasionally makes the NMR spectra almost unobservable, but important information can be derived for the environment of the quadrupolar nuclei. This 'first-order' quadrupolar interaction is generally so large that it is almost impossible to rotate the sample sufficiently rapidly to erase its effect.

It is important that the transition between $+1/2 \leftrightarrow -1/2$ in a nucleus of odd multiple 1/2 spin does not depend on the first-order quadrupolar interaction so that the line shapes of the polycrystalline samples will become sufficiently narrow (a few kHz). In this case, broadening due to the 'second-order' quadrupolar contribution is observed but to a small degree (it is not eliminated) [33,35].

Several nuclei which have relatively small nuclear quadrupole moments have been extensively studied because their line broadening is not so significant and fine structure is usually observed, for example with calcium-43 [139], vanadium-51 in potassium and ammonium metavanadate [35] and manganese-55 in potassium permanganate [27].

Cobalt-59 also has a medium magnitude quadrupolar moment, and MAS NMR has been carried out for the highly symmetric CoL_6-type ligand atom environment, in which the electric field gradient is almost negligible. The difference of the chemical shifts between crystalline phase and aqueous solutions is around several hundred ppm [142]. Several hexanitrocobaltates(III) have been studied by a Russian group [159].

Sodium-23 spectra were reported for complexes with several biochemically important ionophores, crowns and cryptands. Extensive studies have been reported by Tabeta and Saito, and others [36,80,102,103,132,158]. The monensin and tetranactin complexes of Na^+ show similar spectra in the solid state compared with chloroform solution. This reveals the close resemblance of the sodium ion environment in both media; the exchange rate is relatively slow. Other complexes, such as valinomycin or nonactin, showed a remarkable change in chemical shift with signal narrowing, inferring rapid exchange of solvent molecules (mostly in methanol solution).

In the sodide (Na^- anion) containing solids, solid-state NMR expressed the characteristic chemical shift in several crystalline solids of the crown and cryptate complexes. The chemical shift difference for Na^+ is about 50 ppm (low frequency side). MAS NMR spectra of ^{133}Cs and ^{23}Na of the caesium–sodium 18-crown-6 complex revealed the existence of $[Cs^+18C6]Na^-$, and not $[Na^+18C6]Cs^-$ [68].

G. VARIABLE-TEMPERATURE MEASUREMENT. DYNAMIC NMR FOR SOLIDS

It should clearly be interesting to observe MAS NMR spectra as a function of different temperatures, yet variable-temperature MAS NMR is a relatively newly developed technique. This is due to an improvement in mechanical engineering. The sample rotors are designed to spin exactly around the axis oriented 54.7° from the magnetic field direction. This is usually driven by an air-turbine system. The rotor materials are mainly made of plastic polymers, and the mechanical precision was not sufficiently good over the wide temperature range which could provide us with interesting chemical information. Deviation of this angle causes significant line broadening and has prevented detailed study with variable temperature until recently [11,119,120].

The fluxional behaviour of several metal carbonyls, such as $Fe_3(CO)_{12}$ [18,30,116] and $Co_2(CO)_8$ [69], in the solid phase can be studied by carbon-13 MAS NMR with the aid of isotope enrichment. The change of spectral pattern clearly shows the dynamic characteristics of these carbonyls, previously noted with Raman spectroscopy or X-ray crystallography. These stereochemically non-rigid chemical species have usually been studied only in solution, but extension to the solid state can give more precise information in a wider temperature range. The improvement of variable-temperature cell materials (and designs) will widen the applications for this fruitful area.

H. PARAMAGNETIC SOLIDS

Paramagnetic solids, fluxional molecules, and solids with phase transitions can usefully be studied by this modern technique, but the number of such reports has not yet increased. The chemical shift has been assumed to be largely affected by the bulk magnetic susceptibility. Therefore, most solid state NMR studies are limited only to diamagnetic samples. Of course the paramagnetic broadening and contact and dipolar shifts may give rise to complicated spectra which can not easily be analyzed. Moreover, severe line broadening may cause the spectra to be unobservable [153].

Nevertheless, several interesting paramagnetic samples have been successfully studied by CP/MAS NMR. Relaxation time measurements have been applied to the determination of the copper content of soils [75]. A theoretical calculation of the NMR line shape for paramagnetic samples has been reported recently [181].

Praseodymium acetate shows well-resolved multiplets with carbon-13 NMR [67], indicating that there are two different acetate group sites in this crystal.

The two isomorphic Hofmann-type clathrates, $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (diamagnetic) and $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ were also examined by carbon-

13 CP/MAS spectroscopy. The motional characteristics of the guest benzene molecules can clearly be shown by this technique [187]. Other clathrates can be well characterized by the CP/MAS technique for both the guest molecule and host lattice components.

Concerning the well-known copper(II) carboxylate dimer problem, tetrakis-(μ-formato)dicopper(II) bis(pyridine) adduct has been studied by carbon-13 CP/MAS NMR [161] using a 10% isotopically enriched sample. Anti-ferromagnetic spin pairing observed at −181°C causes finely resolved multiplet spectra due to the scalar coupling between two copper nuclei ($I = 3/2$). A significant line broadening and low-frequency side shift was observed at about −100°C [161].

The variable-temperature study of paramagnetic solids can provide much information about amorphous and crystalline phases which have been rather poorly studied until now by NMR spectroscopy.

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