

**ANNUAL REPORTS ON
NMR SPECTROSCOPY**

Volume 10A

ANNUAL REPORTS ON NMR SPECTROSCOPY

Edited by

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VOLUME 10A

1980



ACADEMIC PRESS

A Subsidiary of Harcourt Brace Jovanovich, Publishers

London • New York • Toronto • Sydney • San Francisco

ACADEMIC PRESS INC. (LONDON) LTD.
24-28 Oval Road,
London, NW1 7DX

U.S. Edition Published by

ACADEMIC PRESS INC.
111 Fifth Avenue
New York, New York 10003

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British Library Cataloguing in Publication Data

Annual reports on *NMR* spectroscopy.

Vol. 10A

1. Nuclear magnetic resonance spectroscopy

I. Webb, Graham Alan

541'.28 QD96.N8 68-17678

ISBN 0-12505310-X

ISSN 0066-4103

Printed in Great Britain by J. W. Arrowsmith Ltd.
Bristol BS3 2NT

ANNUAL REPORTS ON

NMR SPECTROSCOPY

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PREFACE

The widespread application of the NMR spectroscopy of "other nuclei" is clearly reflected in the contributions to this volume. As with some earlier members of this series of reports, the present volume is split into two parts.

Volume 10B is the more specific one, dealing with the ^{19}F NMR parameters of various series of compounds. It comprises extensive tabulations of ^{19}F NMR data and serves to update reports in earlier volumes of this series.

The range of topics covered in volume 10A indicates some of the numerous areas of science which are dependent upon NMR as a primary investigative tool. The areas covered include transition metal NMR, ^{13}C NMR applications to synthetic polymers, and some uses of ^{31}P NMR in biochemistry.

All the authors writing for volume 10 are new to Annual Reports and, in welcoming their contributions, I wish to thank all of them for their efforts and patience both in the preparation of their manuscripts and of this volume.

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G. A. WEBB
December 1979

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I. INTRODUCTION

The structures and chemical behaviour of compounds containing metal atoms comprise a major portion of that broad field of human endeavour which still goes under the designation of inorganic chemistry. While the first generation of commercial NMR spectrometers proved to be of greatest utility to the organic chemist because of the emphasis on proton detection, the current generation of pulsed Fourier transform (FT) instruments brings the routine detection of metal atom resonances within the realm of reality. During the developing years of NMR spectroscopy starting about 1950, the proton was the focus of attention because of its high detection sensitivity. Its

limited shielding range of 10 ppm in typical organic compounds, later extended to 25–30 ppm by the hydridic protons in metal hydrides, precluded a simple theoretical interpretation for observed shieldings and led to the development of empirical correlations between structure and chemical shift.

In 1950, Ramsey (111) adapted Van Vleck's quantum-mechanical model (203) for magnetic susceptibility to provide a general theoretical formulation for nuclear shielding, and the appearance of ^{19}F and ^{59}Co spectra with chemical shift ranges of 750 ppm and 14 000 ppm provided an opportunity to test Ramsey's shielding theory on systems sufficiently sensitive to reveal the effects of subtle changes in chemical bonding. While the initial NMR focus on protons with their largely s-orbital* participation in bonding led to the association of increased shielding with increased electron density through a diamagnetic mechanism, the Ramsey treatment of ^{19}F shieldings, where p-orbital participation dominates the chemical bonding, attributed 90% of the observed shielding variation to the paramagnetic term σ_p which measures the orbital angular momentum. The other 10% was attributed to the diamagnetic term σ_d which measures the spherically symmetrical part of the electron distribution and is the putative source of non-hydridic proton chemical shifts.

Transition metals are, by definition, those elements for which the d-orbitals play a significant, if not a dominating, role in chemical bonding. This role becomes manifest in those physical properties sensitive to variations in orbital angular momentum, and nuclear shielding is one of these. Other manifestations are temperature-independent paramagnetism and spin-orbit coupling, both of which are larger for transition metal compounds than for compounds of the Main Group elements. Thus, although other factors enter the picture, it is the d-orbital participation with its large orbital angular momentum contribution that is fundamental to the large chemical shifts undergone both by transition metals themselves and by other atoms covalently bonded to them. The ^{59}Co shielding range of 18 000 ppm reflects the combination of all factors, including d-orbital participation, working together to maximize the variation in nuclear shielding.

The Ramsey theory has been successfully applied to the task of calculating nuclear shieldings in some small molecules. At the stage where even modest molecular dimensions are reached, however, the direct application of the Ramsey theory is made impractical by a number of serious drawbacks summarized recently by Webb. (205) The result has been the adoption of different semi-empirical theoretical models for each nucleus studied, most of them based on the average excitation energy (AEE) method discussed in detail in Section VIII in connection with ^{59}Co shieldings. Jameson and

* Recall that the s, p, and d orbital designations reflect 0, 1, and 2 units of orbital angular momentum.

Gutowsky (204) have provided the only theoretical model to be broadly applied across a range of elements, and it too makes use of the AEE formalism. While it is reasonably successful in rationalizing the observed periodicity in chemical shift ranges for the Main Group elements, it has not been applied with any degree of success to a series of transition metals, nor has its efficacy been tested in the cause of rationalizing the incidence of normal versus inverse halogen dependence.

The value of a theoretical model is directly proportional to the number of different systems to which it can be successfully applied, and hence to the generality of the insight it provides. By this measure, no chemical shift theory has been found to apply more broadly than for two or three elements in atomic number sequence or for three or four elements within a Periodic Group. As more broadly based theories of nuclear shielding begin to take form, the body of chemical shift data for the transition metals must inevitably form the anvil upon which these theories are wrought. The body of data here drawn together and analysed has been selected with this end in view. Relaxation data and coupling constants have been included only where they serve this end or where they comprise the only NMR parameters available on a particular element.

A comprehensive review of the transition metal NMR literature to early 1977 is available. (207) Wehrli (206) has surveyed the recent literature on quadrupolar nuclei, many of which are transition metals, to early 1978. The literature to early 1979 has been surveyed for the present report. During the past two years, the transition metals that have received most study are ^{113}Cd and ^{199}Hg ; this interest stems from their relationship to biologically active molecules, and they have received more detailed coverage than some of the other elements such as ^{59}Co where NMR knowledge is more extensive but less recent.

A. Magnitude of the paramagnetic term

Any theoretical approach to nuclear shielding which rests on a perturbation treatment will involve a diamagnetic (σ_d) and a paramagnetic term (σ_p), with the paramagnetic term being inversely proportional to one or more electronic energy separations in the molecule under consideration. In the absence of sufficiently detailed knowledge of excited-state wavefunctions and energies to enable evaluation of the orbital angular momentum matrix elements between ground and excited states, recourse is had to the AEE approximation which casts the shielding equation in the form:

$$\sigma = \sigma_d + \sigma_p = A - B/\Delta E \quad (1)$$

where ΔE is taken as the value of the AEE. Differences in the theoretical approaches adopted by different workers reside in the method used to

calculate the orbital angular momentum matrix elements contained in the B factor; Ramsey, (111) Griffith and Orgel, (99) Jameson and Gutowsky, (204) and Pople (208) have each introduced different ways of tackling the problem. All these methods have an outcome common to the extent that, as the size of the atom increases, an increasing fraction of its shielding *variation* resides in the paramagnetic term, and for all atoms heavier than lithium σ_p accounts for at least 90% of the observed chemical shift range.* Thus the theory of nuclear shielding for all but the lightest elements must be addressed through the paramagnetic term.

The development of a more broadly based shielding theory requires a homogeneous set of experimental data which compare analogous shielding environments for a range of elements. The first such data set to be assembled was the 1963 shielding ranges observed for Main Group elements and used by Jameson and Gutowsky. (204) While useful in its time, this compilation had two severe limitations. The transition metals, with the highest inherent shielding sensitivities, are not represented. The data set also lacks homogeneity in that paucity of experimental shift data precludes the comparison of analogous environments. The intervening 15 years has seen a growth in shielding data for "other nuclei" to the extent that both of these deficiencies can now be rectified.

In searching for a pair of shielding values with which to measure the sensitivities of different elements, one discovers that chemical combinations with the halogens provide a more extensive set of data than any other. The MCl_4 – MI_4 pairs are particularly useful in that their chemical shifts span a significant proportion of the total shielding range for most elements. The $M^{n+}(aq)$ – M (free atom) pair provides another comparison which, although more limited in extent, provides the benefit of involving an "absolute" shielding reference. Both of these are discussed if data are available in the subsequent sections dealing with the individual elements.

B. Metal atom shielding sensitivities

It has been known for some time that the chemical shifts for analogous compounds of two different elements from the same Periodic Group correlate reasonably well with one another. The plot (210) of $\delta(^{207}\text{Pb})$ vs. $\delta(^{119}\text{Sn})$ for 15 compounds has a slope of 3.0, and the $\delta(^{125}\text{Te})$ vs. $\delta(^{77}\text{Se})$ plot (85) for 14 compounds has a slope of 1.8. A similar comparison (8) shows ^{199}Hg to have a shielding sensitivity 2.9 times that of ^{113}Cd . These comparisons indicate that there is some merit in the concept of an inherent shielding sensitivity for each element.

* The atom-dipole model suggested by Flygare, (209) which gives to σ_d a larger fraction of σ , is not based upon the electronic wavefunctions for the molecule and is therefore incapable of evaluating the explicit contribution of the orbital angular momentum.

[illegible]

Where data for the appropriate iodide compound are missing, the Cl-Br separation has been divided by 0.3 as representative of the typical (Cl-Br)/(Cl-I) ratio. While it would be too much to expect other measures of relative sensitivity to coincide precisely with these values, they provide a more comprehensive set than any other measure, and in most cases comparisons with $M^{n+}(aq)$ -M(free atom) or with particular ligand substituent constants agree within $\pm 20\%$.

The shieldings of all atoms are particularly sensitive to halogen substitution. The ^{13}C shielding patterns for the halogenomethanes received early attention (202) from NMR spectroscopists, and CH_3I was at one stage adopted as the reference compound for ^{13}C chemical shifts because of its position at the extreme low frequency end of the shielding range. The fact that iodine substitution causes large low frequency shifts becomes increasingly obtrusive as the shieldings of additional atoms come under study. Compounds of the type EX_4^{2-} , EX_4^- , EX_4 , and EX_4^+ are formed by

elements from Groups II, III, IV, and V respectively, and for those elements where the data are available, the $\text{ECl}_4\text{--EI}_4$ chemical shift is over half the total shielding range for the element, with the EI_4 compound at or close to the top of the shielding range in every case. The uniformity of this pattern extends to the relative position of the EBr_4 compound which lies to low frequency of ECl_4 , 1/4 to 1/3 of the distance to EI_4 . The relative positions of the resonances for the chloride, bromide, and iodide compounds can be expressed in terms of the $(\text{Cl--Br})/(\text{Cl--I})$ ratio which generally adopts values in the range 0.25 to 0.33. The halogen shielding order $\text{Cl} < \text{Br} \ll \text{I}$ holds for ^{11}B , ^{27}Al , ^{71}Ga , ^{115}In , ^{13}C , ^{29}Si , ^{73}Ge , and ^{119}Sn , and is sufficiently pervasive in other regions of the Periodic Table for compounds containing only one E-X bond, that it has come to be designated the normal halogen dependence (NHD).

For elements where shielding information for the analogous fluoride compound is available, the fluoride shielding pattern is much less consistent. This is not too surprising when one considers the prevalence of anomalous behaviour for the first-row element in each of the Periodic Groups. The fluorides of the Main Group elements generally absorb to low frequency of the chlorides. For ^{11}B the shielding order is $\text{Cl} < \text{F} < \text{Br}$, while for ^{27}Al , ^{29}Si , and ^{119}Sn the order is $\text{Br} < \text{F} < \text{I}$. The normal halogen dependence designation carries with it no implication about the fluoride chemical shift.

Most of the transition metals display normal halogen dependence. In 1971, however, Buslaev reported that the ^{93}Nb nucleus in NbCl_6^- is more highly shielded than that in NbBr_6^- . Shortly thereafter, Kidd, Matthews, and Spinney reported that a similar situation prevails for ^{47}Ti and ^{49}Ti in TiCl_4 and TiBr_4 ; this led to speculation that inverse halogen dependence (IHD) might be a common property of transition metal halides. The information contained in Fig. 1 shows that the incidence of IHD among the transition metals studied to date is restricted to Sc, Ti, V, Nb, Cu, and Ag. The other transition metals to have been tested, W, Mn, Co, Rh, Pt, Zn, Cd, and Hg, all show normal halogen dependence. The distribution of IHD among the transition metals is interesting and may ultimately provide the clue as to the cause of this phenomenon. Adopting the convention that assigns a B-designation to the Sc to Zn Periodic Groups, it is Groups IB, IIIB, IVB, and VB only which show any evidence of IHD. In Group IIB, Zn, Cd, and Hg all show strong evidence of NHD, and in Groups VIB, VIIB, VIIIB, IXB, and XB data for at least one element showing NHD are available.

When we step outside the transition metal area, the situation becomes even more interesting. Groups IIIA, IVA, VA, and VIA all show NHD. In Group IA, however, both the solid alkali halides (154) and the slopes of the concentration plots for aqueous alkali halides (60) show IHD. Little information with which to assess the behaviour of Group IIA elements is available. Some ^9Be shielding studies (51) suggest that beryllium may show

NHD, as do the concentration plots for aqueous $^{43}\text{Ca}^{2+}$ and $^{87}\text{Sr}^{2+}$ salt solutions, (52) but a definitive answer must await further work.

What causes this peculiar reversal of halogen dependence on moving from group to group across the Periodic Table? Since the full scope of the phenomenon has not previously been traced, the current theories of nuclear shielding make no attempt to explain the reversal. It is also clear, however, that no future theoretical development can be regarded as completely successful until it does. A clue to its origin lies with the manner in which the reversal occurs. As we move across the Periodic Table, the halogen dependence does not start off with one sign, gradually diminish in magnitude until it passes through zero, and then increase in magnitude with the opposite sign. Rather it undergoes abrupt sign reversal on passing from one group to the next with no apparent diminution in magnitude.

The valence-shell electron configurations of those atoms exhibiting IHD are s^1 , d^3 , d^4 , d^5 , and $d^{10}s^1$ for the K, Sc, Ti, V, and Cu triads, respectively. These are all electron configurations for which the valence orbital set is *less than half filled*.

The spin-orbit coupling constant is a fundamental atomic parameter the sign of which depends upon whether the valence orbital set is more or less than half filled. (53) For configurations less than half filled, the multiplet resulting from spin-orbit splitting of the term has the component of lowest angular momentum lying lower in energy, while for configurations more than half filled the component of highest angular momentum is more stable. The effect of this magnetic property can be seen in the departure from spin-only value of the magnetic susceptibility of a complex, and in the zero-field splitting observed by ESR spectroscopy. The effect of spin-orbit coupling upon nuclear shielding in diamagnetic compounds has been assessed (116) and has up to now been regarded as relatively unimportant. It is just possible that future considerations of this question may reach a different conclusion.

II. THE SCANDIUM TRIAD

In chemical terms, scandium, yttrium, and lanthanum are considerably more basic than aluminium, and their behaviour resembles that of the alkaline earths rather than that of the transition metals. In chemical combination they form only the M^{III} oxidation state, and the M^{3+} ions show little tendency to form coordination complexes. Their oxides are *not* amphoteric, so the formation of anionic species such as ScCl_4^- is extremely unlikely. Their interactions with counterions in aqueous solution are transitory, and shielding differences which result from these interactions are manifest as variations in the position of a time-averaged resonance line whose position depends upon both the concentration and the static shielding

of the complexed metal ion. All attempts to measure static shieldings for complexes of these metals have been hampered by lack of the appropriate formation constants.

Both ^{45}Sc and ^{139}La have receptivities that make them easier to detect than the alkaline earths. In general their ease of detection is comparable to that of the alkali metals. The information to emerge from the small number of NMR studies carried out on each of these nuclei projects an image similar to that cast by ^{23}Na , ^{39}K , and the other alkali metals, an image based upon concentration dependences, anion effects, preferential solvation, and changes in relaxation times rather than upon chemical shift values assignable to particular metal environments.

TABLE I

Nuclear properties of the scandium triad elements

Nucleus	Spin	Abundance (%)	Quadrupole moment $\cdot 10^{28}$ (m^2)	Usual shielding reference	Receptivity re ^{13}C
^{45}Sc	7/2	100	-0.22	$\text{Sc}^{3+}(\text{aq})$	1710
^{89}Y	1/2	100	0	$\text{Y}^{3+}(\text{aq})$	0.67
^{139}La	7/2	99.9	0.21	—	336

^{89}Y is a spin $I = 1/2$ nucleus and might be expected to yield sharp resonances with relative ease. Its magnetic moment is low, however, so lacking a quadrupolar relaxation mechanism and with only an inefficient magnetic dipolar one, the resonances saturate readily and a special detection technique is used to circumvent this problem.

A. Scandium-45

A precise measurement of the ^{45}Sc magnetic moment has been carried out by Lutz, (193) who identified both the concentration and anion dependence of scandium shieldings and measured the solvent isotope effect between light and heavy water to be $\delta(\text{Sc}^{3+}, \text{H}_2\text{O}) - \delta(\text{Sc}^{3+}, \text{D}_2\text{O}) = 6.2$ ppm. Buslaev *et al.* (190) and Melson *et al.* (191, 192) have extended the earlier work of Lutz to put the anion dependence of aqueous Sc^{3+} shieldings on a quantitative basis. The concentration plots for the chloride, bromide, and perchlorate salts all extrapolate to a common origin at infinite dilution which has been adopted as the $\delta = 0$ reference for ^{45}Sc chemical shifts. At concentrations below 1 molar the plots are reasonably linear with slopes $\delta = -3.6$ ppm M^{-1} for ClO_4^- , $\delta = -2.5$ ppm M^{-1} for Br^- , and $\delta = +0.5$ ppm M^{-1} for Cl^- . At higher concentrations, the plots show some