Magnetic Nonequivalence of Methyl Protons in Metal Isopropoxides

By (MISS) ANITA MEHROTRA and R. C. MEHROTRA*

(Chemical Laboratories, University of Rajasthan, Jaipur-4, India)

Summary N.m.r. spectra of double isopropoxides $[M^1\{M^2(OPr^i)_4\}_3]$ confirm a structure similar to that of tetrameric aluminium isopropoxide and show magnetic nonequivalence of methyl protons in the bridging as well as terminal isopropoxy groups.

ATTEMPTS[1,2] have been made to explain the AB rather than A_2 type spectra of the CH_2 protons in diethyl sulphite,[3–5] acetaldehyde diethyl acetal[4] and cyclopropylhydroxymethyl ethyl ether[4] on the basis of their magnetic nonequivalence. Similarly the nonequivalence of methyl protons in some isopropyl esters has been shown by Bowman and his co-workers[6] and the subject has been reviewed recently.[7]

Shiner and his co-workers[8] first recorded the ^{1}H n.m.r. spectrum of aluminium isopropoxide, for which a tetrameric structure has been proposed.[9] The spectrum consists of a high field doublet (6 terminal OPr^i) and two equal low-field doublets (6 bridging OPr^i), and the nonequivalence of the bridging isopropoxy groups has been ascribed to steric factors. Worrall and his co-workers[10] recently suggested another explanation in terms of asymmetry of the bridging oxygen atoms. Oliver and Worrall[11] have recently found that the methylene protons of both the terminal as well as bridging alkoxy groups in tribenzyloxyaluminium and tris-(4-chlorobenzyloxy)aluminium exhibit magnetic nonequivalence, although the δ_{AB} values are much smaller for the terminal groups which is understandable on the basis of relative distance from the asymmetric centre.

In order to confirm the proposed structure,[12] Oliver and Worrall[14] studied the ^{1}H n.m.r. and mass spectra of the lanthanum derivative, following the synthesis of a number of double isopropoxides of aluminium with lanthanides (La and Pr;[12] Nd, Sm, Dy, and Yb[13]), but the n.m.r. spectrum exhibited only a single methyl doublet at 1·48 p.p.m., suggesting rapid interchange between bridging and terminal isopropoxy groups.

In view of the much smaller radius of scandium and indium, we have synthesised the corresponding double isopropoxides $[\text{M}\{\text{Al}(\text{OPr}^i)_4\}_3]$ and recorded their ^{1}H n.m.r. spectra (60 and 100 MHz) (see Table).

In all these spectra, the areas of the doublets centred at A,B, and (C+D) are roughly in the ratio 1:1:2 with the heights of the doublets at C and D being almost equal.

These spectra are almost identical with that of tetrameric aluminium isopropoxide, except that the doublets due to the methyl protons of the terminal isoproxy groups also appear to split into two almost equal doublets. As expected the δ_{AB} values for the terminal groups are much smaller than those for the bridging ones.

TABLE

Mean τ value for the Me *doublets in the n.m.r. spectra of the metal isopropoxides* (J = 6 Hz *in every case.*)

Compound	Solvent	A	B	C	D	Type of spectrum
$[\text{Sc}\{\text{Al}(\text{OPr}^i)_4\}_3]$	CCl_4	8·52	8·68	8·88	8·91	HA 100
"	"	8·55	8·70	8·92	8·93	A 60
"	$CDCl_3$	8·47	8·63	8·84	8·85	A 60
$[\text{In}\{\text{Al}(\text{OPr}^i)_4\}_3]$	$CDCl_3$	8·52	8·68	—	8·88	A 60
"	"	8·52	8·68	8·87	8·89	HA 100
"	CCl_4	8·52	8·68	8·87	8·89	HA 100
		Bridging		Non-bridging (Terminal)		

These spectra, therefore, fully support the structure proposed[12] for double isopropoxides, $[\text{M}\{\text{Al}(\text{OPr}^i)_4\}_3]$, and also record, for the first time, a new type of splitting for the terminal methyl protons of the isopropoxy groups of metal isopropoxides, which might be expected to be a general phenomenon in high resolution n.m.r. spectra of hindered metal isopropoxides.

Thanks are due to Dr. G. T. Rajjan of R.R.L., Hyderabad and Professor C. C. Patel of the I.I.Sc., Bangalore for the 60 and 100 MHz spectra respectively and to Dr. G. Srivastava for helpful discussions.

(*Received*, 26*th October* 1971; *Com.* 1863.)

---

[1] J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, 1961, **65**, 562.

[2] F. Kaplan and J. D. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 4666.

[3] H. Finegold, *Proc. Chem. Soc.*, 1960, 283.

[4] R. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Nat. Acad. Sci.*, 1961, **47**, 49.

[5] J. G. Pritchard and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 2105.

[6] N. S. Bowman, D. E. Rice, and B. R. Switzer, *J. Amer. Chem. Soc.*, 1965, **87**, 4477.

[7] B. V. Gorkam and G. E. Hall, *Quart. Rev.*, 1968, **22**, 14.

[8] V. J. Shiner, jun., D. Whittaker, and V. P. Fernandez, *J. Amer. Chem. Soc.*, 1963, **85**, 2318.

[9] R. C. Mehrotra, *J. Indian Chem. Soc.*, 1953, **30**, 585; D. C. Bradley, 'Metal Alkoxides,' Advances in Chem. Series, Vol. 23, American Chemical Society, Washington, D.C., 1959, p. 10.

[10] T. N. Huckerby, J. G. Oliver, and I. J. Worrall, *Chem. Comm.*, 1968, 918; J. G. Oliver, P. K. Phillips, and I. J. Worrall, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1609.

[11] J. G. Oliver and I. J. Worrall, *J. Chem. Soc.* (*A*), 1970, 1389.

[12] R. C. Mehrotra and M. M. Agrawal, *Chem. Comm.*, 1968, 469.

[13] M. M. Agrawal, Ph.D. Thesis, University of Rajasthan, Jaipur, India, 1968.

[14] J. G. Oliver and I. J. Worrall, *J. Chem. Soc.* (*A*), 1970, 845.