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## Auto-association in Organometallic Compounds: A Nuclear Magnetic **Resonance Study of Methylcadmium Alkoxides**

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Cadmium chemical shifts and coupling constants have been measured for a series of methylcadmium alkoxides and alkanethiolates using <sup>1</sup>H, <sup>1</sup>H-{<sup>111</sup>Cd}, and <sup>1</sup>H-{<sup>113</sup>Cd} n.m.r. spectroscopy. The results are consistent with all the alkoxides having the same tetrameric structure. Evidence is also presented that the less sterically hindered alkoxides equilibrate slowly to form higher oligomers which are probably hexamers.

CO-ORDINATIVELY unsaturated metallic elements M when covalently bonded to electronegative groups X often auto-associate by forming M-X-M bridges. The n.m.r. properties of M are dictated by the distribution of electrons about it. In suitable cases these properties can be measured and used to investigate structure, as, for example, in recent studies of the auto-association of

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methyltin alkoxides using <sup>1</sup>H-{<sup>119</sup>Sn} n.m.r. spectroscopy.<sup>1</sup> Methylcadmium alkoxides [CdMe(OR)] and thiolates [CdMe(SR)] are also known <sup>2,3</sup> to undergo autoassociation in solution; the resulting species are believed to have the structures (I)—(III) (X = OR, SR). Here we report the results of <sup>1</sup>H, <sup>1</sup>H-{<sup>111</sup>Cd}, and <sup>1</sup>H-{<sup>113</sup>Cd}

- J. D. Kennedy, J.C.S. Perkin II, 1977, 242.
  G. E. Coates and A. Lauder, J. Chem. Soc. (A), 1966, 264.
  E. A. Jeffery and T. Mole, Austral. J. Chem., 1968, 21, 1187.

double resonance experiments on a series of these compounds. These were undertaken in order to delineate the extent of the variations which occur, particularly in cadmium chemical shifts, and to relate them to structural changes.



Previous studies of cadmium nuclear shielding have been limited to the investigation of inorganic cadmium salts in aqueous solution, together with a few simple diorganocadmium compounds.<sup>4-7</sup> Our work more than doubles the number of compounds for which cadmium chemical shifts have been reported, and permits the evaluation of effects within a series of closely related compounds.

## EXPERIMENTAL

Methylcadmium compounds were handled in an inert atmosphere. Dimethylcadmium, b.p. 107 °C, was prepared from methylmagnesium iodide and cadmium chloride in ethoxyethane and purified [to >99.5 mole % (integrated <sup>1</sup>H n.m.r.)] by fractional distillation at atmospheric pressure. Methylcadmium alkoxides and thiolates were prepared in situ in the n.m.r. tubes <sup>2</sup> by the addition of an exactly equimolar amount of thiol or alcohol to dimethylcadmium (30 µl; 0.41 mmol) in benzene (0.50 ml) whereupon methane evolution commenced immediately. With solid alcohols and thiols the sequence of addition was reversed. With the less reactive alcohols gentle warming (water-bath at 60 °C) was used to accelerate the completion of the reaction. With acetylacetone, half the dimethylcadmium remained unchanged, and a white crystalline precipitate, presumably cadmium bis(acetylacetonate), was formed. The similarity of this reaction to that<sup>8</sup> of acetylacetone with dicyclopentadienyltin(II) is noted.

N.m.r. measurements were performed on the benzene solutions using a JEOL C60H instrument equipped for double resonance experiments with an additional coil in the probe. <sup>1</sup>H Spectra were generally recorded in the field sweep mode at 24° and calibrated using audio-frequency sidebands. Frequencies at 12.7 and 13.3 MHz respectively for <sup>1</sup>H-{<sup>111</sup>Cd} and <sup>1</sup>H-{<sup>113</sup>Cd} experiments were supplied by a Schlumberger FS-30 frequency synthesiser, which also controlled the main spectrometer frequency at 60 MHz.

<sup>4</sup> G. E. Maciel and M. Borzo, J.C.S. Chem. Comm., 1973, 394. <sup>5</sup> G. E. Maciel, 'NMR Spectroscopy of Nuclei other than Protons,' eds. T. Axenrod and G. A. Webb, Wiley, New York, 1974, p. 347.

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RESULTS

Compounds are numbered according to Table 1. In general satellites due to the isotopes <sup>111</sup>Cd and <sup>113</sup>Cd (natural abundances 12.9 and 12.3% respectively;  $|{}^{2}J(Cd^{-1}H)| =$ 50-90 Hz) were well resolved at 24° and <sup>1</sup>H-{<sup>111</sup>Cd} and <sup>1</sup>H-{<sup>113</sup>Cd} n.m.r. experiments were straightforward. In benzene solutions of dimethylcadmium (1) the lines in the cadmium spectra were sufficiently sharp for their frequencies to be determined to within  $\pm 1$  Hz thus giving a value of  $1.046\ 084\ 10\ \pm\ 0.000\ 000\ 18$  for the ratio  $\gamma(^{113}Cd)/\gamma(^{111}Cd)$ . This improves by a factor of 10 the precision of the previously reported value  $^9$  of 1.046 083  $\pm$  0.000 003. In the alkoxides these lines were broader due to longer range couplings which reduced the precision, but in the t-butoxide (14) and phenoxide (15)  ${}^{3}J(Cd-O-C-{}^{1}H)$  was absent and  $|^{4}J(Cd-O-C-C-1H)|$  was < ca. 3 Hz; the cadmium resonance frequencies were therefore obtained with this order of accuracy and yielded values for v(113Cd)/v(111Cd) of  $1.046\ 084\ 1\ \pm\ 0.000\ 000\ 8$  and  $1.046\ 084\ 1\ +\ 0.000\ 000\ 4$ respectively indicating the absence of any significant primary isotope effect on cadmium shielding in these systems.

Methylcadmium methoxide (2) was insufficiently soluble at  $24^{\circ}$  and so was examined at  $76^{\circ}$ . The other alkoxides and phenoxides showed a general reversible increase in cadmium shielding of  $+0.10 \pm 0.03$  p.p.m. K<sup>-1</sup> within the range 24-72° [i.e. v(Cd) decreased with increasing temperature]. The change for dimethylcadmium (1) was  $-0.17 \pm 0.05$  p.p.m. K<sup>-1</sup> under the same conditions. A decrease in concentration from the value of 0.8M used in this work also had little effect. All compounds studied here were stable to 76° in benzene solution except compound (11) which decomposed to give a grey suspension above 50°.

The n.m.r. spectra of compounds (7) and (10)—(14)showed that only one species was present. Those of compounds (2)—(6) and (9) however showed that a second component developed over a period of days at 24° (and more rapidly when warmed) at the expense of the original component. For a given alkoxide both species had very similar n.m.r. parameters (Table 1), the proton lines for the developing component being marginally the broader. Heating to 72° did not further broaden the two sets of proton lines, nor did it reversibly change their relative intensities.

The methyl proton resonances of the two alkanethiolates (19) and (20) were broad with no apparent cadmium satellites. However the lines could be sharpened by irradiation at the <sup>111</sup>Cd resonance frequency and the cadmium chemical shifts thus determined to  $\pm 3$  p.p.m. Methylcadmium benzoate (18) had a sharp methyl proton resonance line with no satellites and could not be sharpened further by irradiation at cadmium resonance frequencies. Methylcadmium triphenylmethanethiolate was also prepared but was too insoluble for n.m.r. measurements.

The results are presented in Table 1; for brevity coupling constants  ${}^{2}J(Cd-{}^{1}H)$  are given for  ${}^{111}Cd$  only: those for <sup>113</sup>Cd can be obtained by multiplying by 1.046. Cadmium chemical shifts are given relative to  $CdMe_2$  [(1); neat

- <sup>7</sup> A. D. Cardin, P. D. Ellis, J. D. Odom, and J. W. Howard, J. Amer. Chem. Soc., 1975, 97, 1672.
- K. D. Bos, Thesis, Utrecht, 1976.
  M. P. Klein and J. S. Waugh, *Phys. Rev.*, 1959, **116**, 960.

<sup>&</sup>lt;sup>6</sup> R. J. Kostelnik and A. A. Bothner-By, J. Magnetic Resonance, 1974, 14, 141.

liquid] for which  $\Xi(^{111}Cd)$  and  $\Xi(^{113}Cd)$  were taken to be 21 215 478 and 22 193 173 Hz respectively.  $\Xi$  is the resonance frequency corrected to a field at which the protons in tetramethylsilane resonate at exactly 100 MHz. Note that positive shielding is given a negative sign, and vice versa.

## DISCUSSION

In order to facilitate the assessment of our results, cadmium shieldings previously reported 4-7 are summarized in Table 2. The trends observed parallel ca. 1.9. This is smaller than the gradient of 2.9 in the Figure, but is reasonable in view of the approximations involved. It is however worth noting that in Group IV of the periodic table similar discrepancies arise when carbon, silicon, and tin shieldings are compared in this way.14

For reasons <sup>10</sup> based on analysis of the anisotropic shielding components in methylmercury compounds, the electronic changes arising from the successive replacement of a methyl group on dimethylcadmium by

	N.m.r. parameters of methylcadmium alkoxides and related compounds $a$							
Compound	Relative abundance <sup>ø</sup>	δ(Cd) °	$\delta(^{1}H)-$ (MeCd) <sup>d</sup>	δ( <sup>1</sup> H)- (CdOCH) <sup>d</sup>	$\delta(^{1}H)$ - (CdOC <sub>n</sub> CH) <sup>d, e</sup>	<sup>2</sup> J( <sup>111</sup> Cd- <sup>1</sup> H)  <sup>f,g</sup>	<sup>3</sup> J( <sup>111</sup> Cd- <sup>1</sup> H)  <sup>f, h</sup>	
[CdMe,](1) •	100	0	ca0.5					
[CdMe,] (1) ª	100	-2.9	-0.56			$48.8\pm0.5$		
$\left[ CdMe\left( OMe\right) \right] (2)^{k}$	O 40	$-323\pm6$	$-0.10^{1}$	+3.72		$82.5\pm1$	$9\pm1$	
	D 60	$-323 \pm 7$	$-0.10^{l}$	+3.61		$82.5\pm1$	$9\pm2$	
	m	_	-0.06	+3.60		81	9	
[CdMe(OEt)] (3)	O 50	-293 + 4	-0.045	+3.78	$+1.16 (\beta)$ <sup>n</sup>	$79.5 \pm 0.5$	$7.5\pm0.5$	
	D = 50	-293 + 4	-0.045	+4.08	+1.29 (B) <sup>n</sup>	$79.5 \pm 0.5$	ca. 7 3	
	m	-	-0.08	+3.63		80	7	
$[CdMe(OPr^{n})]$ (4)	O 50	-299.8 + 1	-0.02	$+3.76^{j,n}$	$+0.78(\gamma)$	$79 \pm 2$		
	D 50	$-296.3 \pm 2$	0.00	$+4.12^{j,n}$	$+0.90(\gamma)$	$79 \pm 2$	U	
$\left[CdMe(OBu^{n})\right]$ (5)	O 70	-299.0+1	0.00	+3.82	Þ	$80.3\pm0.5$	$7.5\pm0.5$	
	D 30	$-294.5 \pm 1$	+0.035	+4.16	Þ	$80.4 \pm 0.5$	0	
$[CdMe(OBu^i)]$ (6) <sup>q</sup>	O 30	$-307.1 \pm 1$	0.00	+3.67	+0.88 (y)	$80.9\pm0.5$	$7.5 \pm 0.3$	
	D 70	-303 + 2	+0.05	+3.92	$+1.00(\gamma)$	ca. 81	ca. 7.5 °	
$\left[CdMe(Oneo-C_{5}H_{11})\right]$ (7)	100	-314 + 1	+0.05	+3.80	$+0.90(\gamma)$	$81.2 \pm 0.5$	$7.9 \pm 0.3$	
(CdMeOCH,), CH, (8)	O þ	$-302 \pm 8$	+0.23	+4.30 *	$+1.85$ ( $\beta$ ) *	$80 \pm 4$	0	
	Dρ	$-302 \pm 8$	+0.23 *	+4.30 *	+ 2.09 (β) *	$80 \pm 4$	0	
$[CdMe(OCH_{2}Ph)]$ (9)	O >90	$-312 \pm 2$	-0.315	+4.84		$82.2 \stackrel{-}{\pm} 0.5$	$7.5\pm0.3$	
	D <10	t —	-0.30	+4.98		ca. 82	ca. 7.5	
$[CdMe(OCHPh_{a})]$ (10)	100	$-321.6\pm0.5$	+0.61	u		$84.9 \pm 0.5$	u	
[CdMe(OCPh <sub>s</sub> )] (11)	100	$-329.3 \pm 2$	-0.66			$86.5 \pm 1$		
[CdMe(OPr <sup>i</sup> )] (12)	100	$-271.9 \pm 1$	0.00 v	+4.07	$+1.16 (\beta) n$	$\textbf{78.8} \pm \textbf{0.5}$	$6.1\pm0.3$	
	m	_	-0.05	+4.04	,	78	6	
[CdMe(OBu <sup>s</sup> )] (13)	100	$-274.8\pm1$	0.00	+3.87	$+0.72 (\gamma)$	$77 \pm 1$	$7 \pm 2$	
		_			$+1.21$ ( $\beta$ ) w			
$[CdMe(OBu^t)]$ (14)	100	$-259.1\pm0.5$	+0.045		$+1.66$ ( $\beta$ )	$77.3 \pm 0.5$		
[CdMe(OPh)] (15) z	100	-383.2+0.2	-0.06			89.2 + 0.5		
2 . ,3. ,	m	_	-0.10			90		
$[CdMe\mu-(OPh)(py)]_{2}$ (16) $q.y$	100	$-298 \pm 8$	+0.27*			0		
$[CdMe(OC_{6}H_{3}Me_{2}-2,6)]$ (17)	100	$-381 \pm 8$	-0.45 *			ca. 90 °		
[CdMe(OCOPh)] (18)	100	u	-0.375 *			u		
[CdMe(SPr <sup>i</sup> )] (19)	100	$-31\pm3$	+ 0.09 *	+3.62 *	+1.46 (β)	0	0	
$\left[ CdMe(SBu^{t}) \right] (20)$	100	$-44 \pm 4$	+0.20*		$+2.70$ ( $\beta$ )	0	0	
		_						

<sup>a</sup> Data given for 0.8M solutions in C<sub>6</sub>H<sub>6</sub> at 24° unless otherwise indicated. <sup>b</sup> %; after one week at 24°; O = original component, D = developing component. ° In p.p.m. to low field of [CdMe<sub>2</sub>] (neat liquid):  $\Xi(^{111}Cd) = 21 215 478 \Xi(^{113}Cd) 22 193 173 Hz.$ <sup>d</sup> In p.p.m. to low field of Me<sub>3</sub>Si. °  $\beta$  = alkoxy  $\beta$ -proton;  $\gamma$  = alkoxy  $\gamma$ -proton. f In Hz.  $^{a} f(^{113}Cd-X) = 1.046 \frac{n}{f}(^{112}Cd-X)$ . <sup>k</sup> Mean of values for <sup>113</sup>Cd and <sup>111</sup>Cd. ' Neat liquid. ' Slightly broadened. <sup>k</sup> Saturated solution in C<sub>6</sub>H<sub>6</sub> at 78°. ' $\delta(^{1}H) = 0.00$  at 24°. <sup>m</sup> Data from ref. 2. <sup>n</sup> Sharpened by irradiation at  $\nu(Cd)$ . ° Not well resolved. <sup>p</sup> Not measured. <sup>q</sup> Saturated solution in C<sub>6</sub>H<sub>6</sub>. <sup>r</sup> 6.0  $\pm$  0.2 at 52° (sharp); satellites not resolved at 72°. • Broad. ' Concentration too low to be measured. " No Cd satellites or sharpening with  $\nu(Cd)$  observed. <sup>v</sup> - 0.04 at 62°. " Methyl group. <sup>x</sup> <sup>1</sup>H Lines broaden on heating. <sup>y</sup> In 1: 1 pyridine-benzene solution.

those <sup>10</sup> for mercury shielding, but the overall range is smaller (Figure). This is expected if variations in cadmium and mercury shieldings are dominated by the 'paramagnetic' term of shielding expressions.<sup>11</sup> A simple treatment 12 predicts variations in mercury and cadmium shieldings in analogous compounds to be in the ratio  $[\langle r^{-3} \rangle_{6p(\text{Hg})} / \langle r^{-3} \rangle_{5p(\text{Cd})}]$  where  $\langle r^{-3} \rangle$  is the mean inverse cube of electron-nuclear distance. On the basis of literature data 12,13 an estimate of this factor is <sup>10</sup> J. D. Kennedy and W. McFarlane, J.C.S. Faraday II, 1976, 1653.

 <sup>11</sup> N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699.
 <sup>12</sup> C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714.

<sup>13</sup> R. G. Barnes and W. E. Smith, Phys. Rev., 1953, 93, 95.

increasingly electronegative substituents should result in progressively increased shielding of the cadmium nucleus. This is confirmed by our results for the methylcadmium alkoxides and phenoxides (Table 1). The increase in the coupling constants  $|^{2}J(^{111}Cd^{-1}H)|$  is also as expected for methylmetallic compounds and can be rationalised in terms of changes in bonding-orbital s-character and effective nuclear charge.<sup>3,15-17</sup>

<sup>14</sup> W. McFarlane and R. J. Wood, J. Organometallic Chem., 1972, **40**, C17. <sup>15</sup> J. R. Ho

J. R. Holmes and H. D. Kaesz, J. Amer. Chem. Soc., 1961, 83, 3903. <sup>16</sup> D. M. Grant and W. M. Litchman, J. Amer. Chem. Soc.,

1965, **87**, 3994.

<sup>17</sup> J. D. Kennedy and W. McFarlane, J.C.S. Dalton, 1976, 1219.

TABLE 1

Changes in the co-ordination number of a metal modify its electronic distribution and in tin compounds for example this produces large changes in the <sup>119</sup>Sn chemical shift <sup>1</sup> and in the coupling constants involving tin.<sup>15,16</sup> Cadmium n.m.r. parameters have not been investigated in this context, although oxygen donors appear to increase the shielding (Table 2) both when the co-ordination number remains unchanged [*e.g.* compounds (15) and (16)] and when it increases (*e.g.* [CdMe<sub>2</sub>] in THF, Table 2). In the methylcadmium alkoxides,

## TABLE 2

Cadmium chemical shifts a

Compound	Conditions	δ(Cd)/p.p.m.	Ref.
[CdMe,]	Neat	0 0	
	1.0м in С <sub>в</sub> Н <sub>в</sub>	+2.0	7
	1.0м in THF	-66.5	7
	1.0m in cyclo-C <sub>6</sub> H <sub>12</sub>	+34.7	7
[CdEtMe]	1 : 1 mixture of neat	-49.9	7
	[CdMe <sub>2</sub> ] and [CdEt <sub>2</sub> ]		
[CdEt <sub>2</sub> ]	Neat	-99.7	7
[CdPrn,]	Neat	-138.6	7
[CdBun <sub>2</sub> ]	Neat °	-153.8	6 "
[CdPh <sub>2</sub> ]	1.0м in p-dioxan	-314.1	7
[Cd(ClO <sub>4</sub> ) <sub>2</sub> ]	0.1м in H <sub>2</sub> O	-642.9 <sup>d</sup>	4 ª
$[Cd(SO_4)_2]$	$0.1 \mathrm{M}$ in $\mathrm{H}_{2}\mathrm{O}$	-642.9 d,e	6 a
$[Cd(NO_3)_2]$	$0.1 \text{ M}$ in $H_2O$	-644.7 f	6 4
	$4.0 \mathrm{M}$ in $\mathrm{H_2O}$	-706.8 <sup>f</sup>	6 a
[CdCl <sub>2</sub> ]	$0.1 \text{ m in H}_2 \text{O}$	-586.2 "	6 a
	5.0м in H <sub>2</sub> O	-512.0 g	6 a
[CdBr <sub>2</sub> ]	0.1м in H <sub>2</sub> O	- 580.0 g	6 a
	3.0м in H <sub>2</sub> O	$-529.7$ $^{g}$	6 a
$[CdI_2]$	0.1м in H <sub>2</sub> O	-584.2 g	6 "
[Cd(SCN) <sub>2</sub> ]	$0.2M$ in $D_2O$	-582.8	7
$[Cd(CN)_{4}]^{2-}$	1.0м in D <sub>2</sub> O	-133.1	7
$[Cd(Mn(CO)_5)_2]$	0.8м in MeOH	-90.9	7
CdCl <sub>2</sub> (NH <sub>3</sub> ) <sub>6</sub> ]	0.015м in 1 : 1 NH -D.O	-368.6	7
	$10 \text{ min} 1 \cdot 1$	- 354 6	7
	NH-D-O	00110	•
Cd <sup>2+</sup>	Infinite dilution in	-642.8	6 a
-	H <sub>•</sub> O		
Cd <sup>II</sup> EDTA	0.3м in dilute	-490.2 <sup>h</sup>	This
	aqueous NH₄OH		work

<sup>a</sup> To low field of Me<sub>2</sub>Cd. Values from refs. 4 and 6 have been calculated on the basis <sup>7</sup> that  $\delta(Cd)$  in  $0.1 \text{M} [Cd(ClO_4)_2]$  is 642.93 p.p.m. to high field of  $[CdMe_2]$ . <sup>b</sup> Considerable variation with both donating and non-donating solvents.<sup>7</sup> <sup>c</sup> Presumably. <sup>d</sup> Small increase in shielding (<ca. 6 p.p.m.) on concentration to 3M. <sup>e</sup> More shielded with oxygen donor ligands; more deshielded with nitrogen donor ligands; strongly deshielded with sulphur donor ligands.<sup>6</sup> <sup>f</sup> Approximately linear variation between these extremes. <sup>e</sup> Cycloidal variation with concentration. <sup>h 190</sup>Hg in Hg<sup>IIE</sup>DTA under the same conditions resonates at  $-1660 \pm 5$  p.p.m. relative to [HgMe<sub>2</sub>].

the <sup>111</sup>Cd n.m.r. parameters should therefore readily distinguish the three-co-ordinate dimeric structure (I; X = OR) from the four-co-ordinate species (II) and (III). There is in fact significant variation of these parameters within the series of alkoxides (Table 1).

Successive replacement of alkoxy  $\alpha$ -hydrogens by methyl groups results in successive <sup>111</sup>Cd shielding decrements of *ca.* 20 p.p.m. [*e.g.* compounds (2), (3), (12), and (14)]. The sign of these changes is that anticipated on the basis of changes in electron imbalance <sup>10,12</sup> in the metal orbitals arising from inductive electron release from the alkoxy-groups. A similar rationalisation may be applied to the shielding increments of *ca.* 25 p.p.m. observed for the pairs of compounds (3), (9); (4), (10); and (5), (11). The changes observed on replacement of alkoxy- $\beta$ -hydrogens by methyl groups [compounds (3), (4), (6), and (7)] however occur in the opposite sense to that expected on this basis. There are therefore probably additional contributions to the cadmium nuclear shielding similar to those observed for mercury shielding in symmetrical diorganomercury compounds.<sup>10,18</sup> In these, marked shielding and deshielding effects are associated with hydrogen atoms respectively  $\beta$  and  $\gamma$  to the *metal* atom,



Mercury-199 versus cadmium-111 chemical shifts for comparable compounds: A,  $[HgMe_2]$  (neat liquid) and  $[CdMe_2]$  (neat liquid); B,  $[HgEt_2]$  (neat liquid) and  $[CdEt_2]$  (neat liquid); C,  $[HgPh_2]$  (0.2M in THF) and  $[CdPh_2]$  (1.0M in dioxan); D,  $[HgCl_2]$  (1.39M in EtOH) and  $[CdCl_2]$  (5.0M in  $H_2O$ ). Values taken from refs. 3, 4, 5, and 10.

and there is a general shielding effect associated with adjacent unsaturated entities.

The variations in cadmium-proton coupling constants can also be correlated with the inductive effects of the alkoxy-groups. Increased electron withdrawal results in an increased effective nuclear charge and would lead to  $^{3,15-17}$  an increase in  $|^{2}J(^{111}Cd^{-1}H)|$  as is observed [*e.g.* compounds (9)--(11)]. Where observable the changes in  $|^{3}J(^{111}Cd^{-1}H)|$  also occur in the same sense, but may be affected by unequal rotamer populations when the alkoxy-group is bulky. It is pertinent in this



respect that  $|{}^{3}J({}^{111}Cd^{-1}H)|$  in compound (7) changes reversibly from 7.9 at 24 to 6.0 Hz at 52°.

At high temperatures, the coupling  ${}^{3}J({}^{111}Cd-O-C-{}^{1}H)$  is retained and there is no change in the other cadmium n.m.r. parameters. In contrast to the methyltin alkoxides,<sup>1</sup> therefore, the methylcadmium alkoxides do

<sup>18</sup> A. P. Tupčiauskas, N. M. Sergeyev, Y. A. Ustynyuk, and A. N. Kashin, J. Magnetic Resonance, 1972, 7, 124. not exist in rapid dynamic equilibrium. The steady variation of the cadmium chemical shift and coupling constant with the inductive effects of the substituents therefore implies that the methylcadmium alkoxides studied here all have the same skeletal structure. In particular the differences between the t-butoxide (14), thought to be dimeric<sup>2</sup> [structure (I)], and the isopropoxide (12), thought to be tetrameric<sup>2,3</sup> [structure (II)], are no greater than those between the isopropoxide (12) and the ethoxide (3), both thought to be tetrameric.<sup>2,3</sup>

In the tetramer (II) each alkoxy-group is attached to three chemically equivalent cadmium atoms. The combined natural abundances of <sup>111</sup>Cd and <sup>113</sup>Cd amount to 25.2% and for this structure, therefore, each line due to the alkoxy  $\alpha$ -protons in the n.m.r. spectrum will be a 0.5:7:44:100:44:7:0.5 multiplet due to coupling  ${}^{3}J({}^{111,113}Cd^{-1}H)$ . The corresponding lines for the dimer (I) would be split into 2.5:32:100:32:2.5 multiplets. On this basis Jeffery and Mole have concluded that compounds (3) and (13) are probably tetrameric,<sup>3</sup> and we have reached similar conclusions for compounds (7) and (9). In these, other species are at a minimum and the alkoxy  $\alpha$ -proton resonances would be effectively singlets in the absence of spin-1/2 cadmium nuclei. The cadmium proton coupling is therefore well resolved and the multiplet intensities exclude the dimeric structure (I).

We therefore conclude that the methylcadmium alkoxides examined here are probably all tetrameric in nature and that there is no reason on the basis of n.m.r. measurements to exclude the t-butoxide (14) from this generalisation. The zinc analogue is tetrameric,<sup>19</sup> and examination of models shows that there would be no steric inhibition due to the large alkoxy-group.

The formation of a second species for those alkoxides with smaller substituents [compounds (2)—(6) and (9)] is interesting. The similarity of n.m.r. parameters implies structural similarity, and may be explained by a hexameric species (III). In this the cadmium and oxygen atoms still retain their co-ordination number of four. The formation of (III) would require initial dissociation of the tetramer (II) and the slowness of the process is consistent with the observed kinetic stability of the tetramers. Methylcadmium propane-2-thiolate (19) is reported to be hexameric in benzene solution,<sup>2</sup> but lack of sufficient comparison n.m.r. data precludes a profitable discussion.

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