

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 ^1H , $^1\text{H}\text{-}\{^{111}\text{Cd}\}$, and $^1\text{H}\text{-}\{^{113}\text{Cd}\}$ 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

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

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¹ J. D. Kennedy, *J.C.S. Perkin II*, 1977, 242.

² G. E. Coates and A. Lauder, *J. Chem. Soc. (A)*, 1966, 264.

³ E. A. Jeffery and T. Mole, *Austral. J. Chem.*, 1968, **21**, 1187.

liquid] for which $\Xi(^{111}\text{Cd})$ and $\Xi(^{113}\text{Cd})$ were taken to be 21 215 478 and 22 193 173 Hz respectively. Ξ 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 reported⁴⁻⁷ 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 reasons¹⁰ 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

TABLE I
N.m.r. parameters of methylcadmium alkoxides and related compounds^a

Compound	Relative abundance ^b	$\delta(\text{Cd})^c$	$\delta(^1\text{H})$ - (MeCd) ^d	$\delta(^1\text{H})$ - (CdOCH) ^d	$\delta(^1\text{H})$ - (CdOC _n CH) ^{d,e}	$ ^2J(^{111}\text{Cd}-^1\text{H}) ^{f,g}$	$ ^3J(^{111}\text{Cd}-^1\text{H}) ^{f,h}$
[CdMe ₂](1) ⁱ	100	0	<i>ca.</i> -0.5				
[CdMe ₂](1) ^a	100	-2.9	-0.56			48.8 ± 0.5	
[CdMe(OMe)] (2) ^k	O 40	-323 ± 6	-0.10 ⁱ	+3.72		82.5 ± 1	9 ± 1
	D 60	-323 ± 7	-0.10 ⁱ	+3.61		82.5 ± 1	9 ± 2
	<i>m</i>		-0.06	+3.60		81	9
[CdMe(OEt)] (3)	O 50	-293 ± 4	-0.045	+3.78	+1.16 (β) ⁿ	79.5 ± 0.5	7.5 ± 0.5
	D 50	-293 ± 4	-0.045	+4.08	+1.29 (β) ⁿ	79.5 ± 0.5	<i>ca.</i> 7.7 ^j
	<i>m</i>		-0.08	+3.63		80	7
[CdMe(OPr ⁿ)] (4)	O 50	-299.8 ± 1	-0.02	+3.76 ^{j,n}	+0.78 (γ)	79 ± 2	<i>o</i>
	D 50	-296.3 ± 2	0.00	+4.12 ^{j,n}	+0.90 (γ)	79 ± 2	<i>o</i>
[CdMe(OBu ⁿ)] (5)	O 70	-299.0 ± 1	0.00	+3.82	<i>p</i>	80.3 ± 0.5	7.5 ± 0.5
	D 30	-294.5 ± 1	+0.035	+4.16	<i>p</i>	80.4 ± 0.5	<i>o</i>
[CdMe(OBu ^t)] (6) ^q	O 30	-307.1 ± 1	0.00	+3.67	+0.88 (γ)	80.9 ± 0.5	7.5 ± 0.3
	D 70	-303 ± 2	+0.05	+3.92	+1.00 (γ)	<i>ca.</i> 81	<i>ca.</i> 7.5 ^o
[CdMe(Oneo-C ₆ H ₁₁)] (7)	100	-314 ± 1	+0.05	+3.80	+0.90 (γ)	81.2 ± 0.5	7.9 ± 0.3
[(CdMeOCH ₂) ₂ CH ₂] (8)	O <i>p</i>	-302 ± 8	+0.23 ^s	+4.30 ^s	+1.85 (β) ^s	80 ± 4	<i>o</i>
	D <i>p</i>	-302 ± 8	+0.23 ^s	+4.30 ^s	+2.09 (β) ^s	80 ± 4	<i>o</i>
[CdMe(OCH ₂ Ph)] (9)	O >90	-312 ± 2	-0.315	+4.84		82.2 ± 0.5	7.5 ± 0.3
	D <10	<i>t</i>	-0.30	+4.98		<i>ca.</i> 82	<i>ca.</i> 7.5
[CdMe(OCHPh ₂)] (10)	100	-321.6 ± 0.5	+0.61	<i>u</i>		84.9 ± 0.5	<i>u</i>
[CdMe(OCPh ₃)] (11)	100	-329.3 ± 2	-0.66			86.5 ± 1	
[CdMe(OPr ^t)] (12)	100	-271.9 ± 1	0.00 ^v	+4.07	+1.16 (β) ⁿ	78.8 ± 0.5	6.1 ± 0.3
	<i>m</i>		-0.05	+4.04		78	6
[CdMe(OBu ^o)] (13)	100	-274.8 ± 1	0.00	+3.87	+0.72 (γ)	77 ± 1	7 ± 2
					+1.21 (β) ^w		
[CdMe(OBu ^t)] (14)	100	-259.1 ± 0.5	+0.045		+1.66 (β)	77.3 ± 0.5	
[CdMe(OPh)] (15) ^z	100	-383.2 ± 0.2	-0.06			89.2 ± 0.5	
	<i>m</i>		-0.10			90	
[CdMe _μ -(OPh)(py)] ₂ (16) ^{q,v}	100	-298 ± 8	+0.27 ^s			<i>o</i>	
[CdMe(OC ₆ H ₅ Me ₂ -2,6)] (17)	100	-381 ± 8	-0.45 ^s			<i>ca.</i> 90 ^o	
[CdMe(OCOPh)] (18)	100	<i>u</i>	-0.375 ^w			<i>u</i>	
[CdMe(SPr ^t)] (19)	100	-31 ± 3	+0.09 ^s	+3.62 ^s	+1.46 (β)	<i>o</i>	<i>o</i>
[CdMe(SBu ^t)] (20)	100	-44 ± 4	+0.20 ^s		+2.70 (β)	<i>o</i>	<i>o</i>

^a Data given for 0.8M solutions in C₆H₆ at 24° unless otherwise indicated. ^b %; after one week at 24°; O = original component, D = developing component. ^c In p.p.m. to low field of [CdMe₂] (neat liquid): $\Xi(^{111}\text{Cd}) = 21\,215\,478$ $\Xi(^{113}\text{Cd}) = 22\,193\,173$ Hz. ^d In p.p.m. to low field of Me₄Si. ^e β = alkoxy β-proton; γ = alkoxy γ-proton. ^f In Hz. ^g $^nJ(^{113}\text{Cd}-\text{X}) = 1.046$ $^nJ(^{111}\text{Cd}-\text{X})$. ^h Mean of values for ¹¹³Cd and ¹¹¹Cd. ⁱ Neat liquid. ^j Slightly broadened. ^k Saturated solution in C₆H₆ at 78°. ^l $\delta(^1\text{H}) = 0.00$ at 24°. ^m Data from ref. 2. ⁿ Sharpened by irradiation at $\nu(\text{Cd})$. ^o Not well resolved. ^p Not measured. ^q Saturated solution in C₆H₆. ^r 6.0 ± 0.2 at 52° (sharp); satellites not resolved at 72°. ^s Broad. ^t Concentration too low to be measured. ^u No Cd satellites or sharpening with $\nu(\text{Cd})$ observed. ^v -0.04 at 62°. ^w Methyl group. ^z ¹H Lines broaden on heating. ^y In 1:1 pyridine-benzene solution.

those¹⁰ 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.¹¹ A simple treatment¹² 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

¹⁰ J. D. Kennedy and W. McFarlane, *J.C.S. Faraday II*, 1976, 1653.

¹¹ N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699.

¹² C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714.

¹³ 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 $|^2J(^{111}\text{Cd}-^1\text{H})|$ is also as expected for methylmetallic compounds and can be rationalised in terms of changes in bonding-orbital *s*-character and effective nuclear charge.^{3,15-17}

¹⁴ W. McFarlane and R. J. Wood, *J. Organometallic Chem.*, 1972, **40**, C17.

¹⁵ J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 3903.

¹⁶ D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, 1965, **87**, 3994.

¹⁷ J. D. Kennedy and W. McFarlane, *J.C.S. Dalton*, 1976, 1219.

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 ^{119}Sn chemical shift¹ and in the coupling constants involving tin.^{15,16} 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.* $[\text{CdMe}_2]$ in THF, Table 2). In the methylcadmium alkoxides,

TABLE 2
Cadmium chemical shifts^a

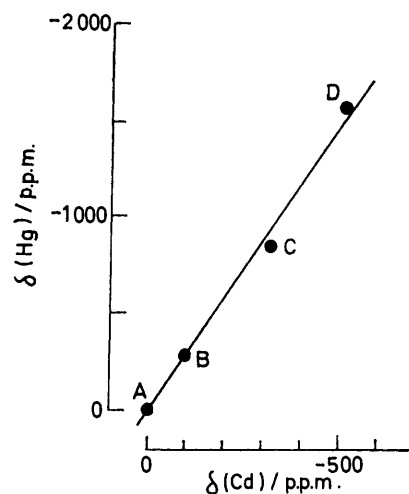
Compound	Conditions	$\delta(\text{Cd})/\text{p.p.m.}$	Ref.
$[\text{CdMe}_2]$	Neat	0 ^b	
	1.0M in C_6H_6	+2.0	7
	1.0M in THF	-66.5	7
	1.0M in cyclo- C_6H_{12}	+34.7	7
$[\text{CdEtMe}]$	1 : 1 mixture of neat $[\text{CdMe}_2]$ and $[\text{CdEt}_2]$	-49.9	7
$[\text{CdEt}_2]$	Neat	-99.7	7
$[\text{CdPr}^n_2]$	Neat	-138.6	7
$[\text{CdBu}^n_2]$	Neat ^c	-153.8	6 ^a
$[\text{CdPh}_2]$	1.0M in <i>p</i> -dioxan	-314.1	7
$[\text{Cd}(\text{ClO}_4)_2]$	0.1M in H_2O	-642.9 ^d	4 ^a
$[\text{Cd}(\text{SO}_4)_2]$	0.1M in H_2O	-642.9 ^{d,e}	6 ^a
$[\text{Cd}(\text{NO}_3)_2]$	0.1M in H_2O	-644.7 ^f	6 ^a
$[\text{CdCl}_2]$	0.1M in H_2O	-586.2 ^g	6 ^a
	5.0M in H_2O	-512.0 ^g	6 ^a
$[\text{CdBr}_2]$	0.1M in H_2O	-580.0 ^g	6 ^a
	3.0M in H_2O	-529.7 ^g	6 ^a
$[\text{CdI}_2]$	0.1M in H_2O	-584.2 ^g	6 ^a
$[\text{Cd}(\text{SCN})_2]$	0.2M in D_2O	-582.8	7
$[\text{Cd}(\text{CN})_4]^{2-}$	1.0M in D_2O	-133.1	7
$[\text{Cd}(\text{Mn}(\text{CO})_5)_2]$	0.8M in MeOH	-90.9	7
$\text{CdCl}_2(\text{NH}_3)_6$	0.015M in 1 : 1 $\text{NH}_3\text{-D}_2\text{O}$	-368.6	7
	1.0M in 1 : 1 $\text{NH}_3\text{-D}_2\text{O}$	-354.6	7
	$\text{NH}_3\text{-D}_2\text{O}$		
Cd^{2+}	Infinite dilution in H_2O	-642.8	6 ^a
Cd^{II} EDTA	0.3M in dilute aqueous NH_4OH	-490.2 ^h	This work

^a To low field of Me_2Cd . Values from refs. 4 and 6 have been calculated on the basis⁷ that $\delta(\text{Cd})$ in 0.1M $[\text{Cd}(\text{ClO}_4)_2]$ is 642.93 p.p.m. to high field of $[\text{CdMe}_2]$. ^b Considerable variation with both donating and non-donating solvents. ^c Presumably. ^d Small increase in shielding ($<ca.$ 6 p.p.m.) on concentration to 3M. ^e More shielded with oxygen donor ligands; more deshielded with nitrogen donor ligands; strongly deshielded with sulphur donor ligands. ^f Approximately linear variation between these extremes. ^g Cycloidal variation with concentration. ^h ^{199}Hg in $\text{Hg}^{II}\text{EDTA}$ under the same conditions resonates at $-1\ 660 \pm 5$ p.p.m. relative to $[\text{HgMe}_2]$.

the ^{111}Cd n.m.r. parameters should therefore readily distinguish the three-co-ordinate dimeric structure (I; $\text{X} = \text{OR}$) 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 α -hydrogens by methyl groups results in successive ^{111}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^{10,12} 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 com-

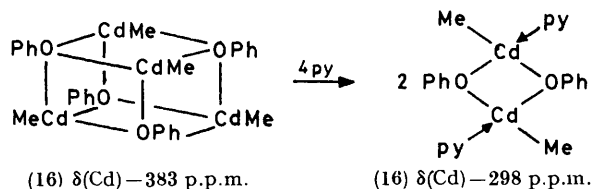
pounds (3), (9); (4), (10); and (5), (11). The changes observed on replacement of alkoxy- β -hydrogens by methyl groups [compounds (3), (4), (6), and (7)] however occur in the opposite sense to that expected on this basis. There are therefore probably additional contributions to the cadmium nuclear shielding similar to those observed for mercury shielding in symmetrical diorganomercury compounds.^{10,18} In these, marked shielding and deshielding effects are associated with hydrogen atoms respectively β and γ to the *metal* atom,



Mercury-199 versus cadmium-111 chemical shifts for comparable compounds: A, $[\text{HgMe}_2]$ (neat liquid) and $[\text{CdMe}_2]$ (neat liquid); B, $[\text{HgEt}_2]$ (neat liquid) and $[\text{CdEt}_2]$ (neat liquid); C, $[\text{HgPh}_2]$ (0.2M in THF) and $[\text{CdPh}_2]$ (1.0M in dioxan); D, $[\text{HgCl}_2]$ (1.39M in EtOH) and $[\text{CdCl}_2]$ (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 $|^3J(^{111}\text{Cd-}^1\text{H})|$ as is observed [*e.g.* compounds (9)–(11)]. Where observable the changes in $|^3J(^{111}\text{Cd-}^1\text{H})|$ 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 $|^3J(^{111}\text{Cd-}^1\text{H})|$ in compound (7) changes reversibly from 7.9 at 24 to 6.0 Hz at 52°.

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

¹⁸ A. P. Tupčiauskas, N. M. Sergejev, 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 dimeric² [structure (I)], and the isopropoxide (12), thought to be tetrameric^{2,3} [structure (II)], are no greater than those between the isopropoxide (12) and the ethoxide (3), both thought to be tetrameric.^{2,3}

In the tetramer (II) each alkoxy-group is attached to three chemically equivalent cadmium atoms. The combined natural abundances of ¹¹¹Cd and ¹¹³Cd amount to 25.2% and for this structure, therefore, each line due to the alkoxy α -protons in the n.m.r. spectrum will be a 0.5 : 7 : 44 : 100 : 44 : 7 : 0.5 multiplet due to coupling $^3J(^{111,113}\text{Cd}-^1\text{H})$. 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,³ and we have reached similar conclusions for compounds (7) and (9). In these, other species are at a minimum and the alkoxy α -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,¹⁹ 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,² but lack of sufficient comparison n.m.r. data precludes a profitable discussion.

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¹⁹ G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1965, 1870.