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The synthesis and spectroscopic characterization of bis(γ-methoxypropyl) cadmium

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Abstract

The preparation of the hitherto-unknown compound $(CH_3O(CH_2)_3)_2Cd$ is reported. It is a colourless oil, which has been shown by mass spectrometry to vaporize without decomposition. A thorough vibrational and multinuclear magnetic resonance study suggests strongly that there is no internal coordination of the O atoms to the Cd atom, whereas such coordination is observed in the zinc-containing analogue.

Key words: Cadmium; MOCVD; Main group metals; Infrared spectroscopy; Nuclear magnetic resonance

1. Introduction

We are currently preparing a range of compounds which may be useful for the production of the semiconductor materials CdS and CdSe [1,2]. One of our aims is to find precursors to reduce or eliminate the problem of "pre-reaction" which plagues the production of these materials by metal–organic chemical vapour deposition (MOCVD) [3]. A possible means of achieving this end is to use, as the cadmium-containing precursor, an organometallic compound in which the organic groups contain donor atoms at such positions that they may coordinate intramolecularly to the cadmium atom which could reduce the reactivity at the cadmium centre and so inhibit pre-reaction.

The compound $(CH_3O(CH_2)_3)_2Zn$ has previously been made, and by spectroscopic [4] and gas electron diffraction measurements [5] it has been shown that there is coordination between the O and Zn atoms. Our aim in the present work was to synthesize the cadmium-containing analogue $(CH_3O(CH_2)_3)_2Cd$ (**A**) and by thorough spectroscopic investigation to establish the presence or absence of intramolecular coordination between the O and Cd atoms. We also examined the possible use of **A** as a precursor for use in MOCVD by investigating its volatility and thermal stability.

2. Experimental section

As the first step, 1-chloro-3-methoxypropane ($CH_3O(CH_2)_3Cl$) was synthesized as described previously by McEwen *et al.* [6]. Thus, CH_3I (142 g, 1.0 mol) and $Cl(CH_2)_3OH$ (47 g, 0.5 mol) were heated at 0°C with powdered NaH (24 g, 1.0 mol) in dry tetrahydrofuran solution under argon. The mixture was stirred at room temperature overnight, and unchanged NaH was destroyed by cautious addition of 150 ml of water during 2 h. The organic layer was separated and dried over anhydrous Na_2SO_4, and the solvent was distilled off. The identity and purity of the 1-chloro-3-methoxypropane were confirmed by a recording of its ^1H and ^{13}C NMR and IR spectra. The yield was 88%.

Under argon a solution of $CH_3O(CH_2)_3Cl$ (24 g, 0.22 mol) in 50 ml of Et_2O was added to an ethereal slurry of coarse magnesium powder (5.3 g, 0.22 mol) containing a crystal of I_2. The mixture was stirred at room temperature for 12 h to allow formation of the Grignard reagent $CH_3O(CH_2)_3MgCl$. The Grignard reagent was then treated with a deficiency of anhydrous $CdCl_2$ (18.4 g, 0.1 mol) in ether under argon. The mixture was stirred for 12 h and the solution then filtered through a sintered glass frit on a vacuum line.

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A (yield, 40%) was separated from the solvent by trap-to-trap distillation on the vacuum line. The product was stirred in an ampoule fitted with a Young's greaseless tap.

3. Results and discussion

Compound A is a colourless oil. It has considerable thermal stability, showing little sign of rapid decomposition when heated to 120°C. It decomposes slowly, during several months, at room temperature, to give a deposit of metallic cadmium and gaseous products. Its volatility is similar to that of $((CH_3)_2N(CH_2)_3)_2Cd$ [7], *i.e.* about 0.1 Torr at 100°C. It was subjected to a thorough spectroscopic investigation as detailed below.

3.1. Mass spectrometry

It is clear from its mass spectrum that A sublimes without decomposition. Weak parent ion peaks are present at around $m/e = 258$, with a cluster of peaks of stronger intensity corresponding to A^+ less one $CH_3O(CH_2)_3$ group at around $m/e = 185$. Peaks corresponding to the various isotopes of Cd^+ are present around $m/e = 112$. Ions at lower m/e values may be assigned to organic fragments. This behaviour in the mass spectrometer is entirely in line with that of dialkylcadmium compounds such as $(CH_3)_2Cd$ and $(CH_3CH_2)_2Cd$ [8].

3.2. IR and raman spectra

There is a strong correlation between the IR (vapour or solid at 77 K) and Raman (liquid) spectra of A. When allowances are made for small variations in frequency due to the change of phase, it is apparent that most of the IR absorptions present in the spectrum of solid A have counterparts in Raman scattering from liquid A. The exception to this rule is in the low frequency region associated with ν(C–Cd–C) vibrations. Here there is an intense Raman line at 457 cm^{-1}, which clearly arises from the ν_{sym}(C–Cd–C) vibration [9,10]. This feature has no counterpart in the IR spectrum; instead an IR band of weak to medium intensity is seen near 511 cm^{-1}, and this is assigned to the ν_{asym}(C–Cd–C) vibration [9,10]. There is no sign of any Raman scattering at this frequency. This observation is in accord with high local symmetry around the cadmium atom and is consistent with a linear C–Cd–C arrangement. It is not consistent with a structure involving internal coordination of O to Cd for which, on symmetry grounds, both ν_{asym} and ν_{sym} of the C–Cd–C–fragment would be IR and Raman active. Such a situation is observed for the adduct $(CH_3)_2Cd \cdot 2,2'$-bipyridyl, for which bands in the Raman spectrum at 440 and 461 cm^{-1} are assigned to ν_{sym} and ν_{asym}(C–Cd–C) respectively [11]. There is no sign, in the vibrational spectra, of any bands arising from ν(Cd–O) vibrations in A.

TABLE 1. Chemical shifts of resonances the ^{1}H nuclear magnetic resonance spectra of $CH_3O(CH_2)_3Cl$, $CH_3O(CH_2)_2CH_3$ and $(CH_3O(CH_2)_3)_2Cd$ (A)

$CH_3O(CH_2)_3Cl$ δ (ppm)	$CH_3O(CH_2)_2$ CH_3 δ(ether) (ppm)	$(CH_3O(CH_2)_3)_2$ Cd δ(A) (ppm)	$\Delta = \delta(A) -$ δ(ether) (ppm)
3.34 (t) (α)	0.88 (t) (α)	0.46 (t) (α)	−0.42
1.67 (q) (β)	1.52 (sx) (β)	2.22 (q) (β)	+0.70
3.17 (t) (γ)	3.16 (t) (γ)	3.14 (t) (γ)	−0.02
3.03 (s) (δ)	3.14 (s) (δ)	3.08 (s) (δ)	−0.06

3.3. Nuclear magnetic resonance spectra

In Table 1 are listed the chemical shifts of the ^{1}H nuclear magnetic resonance (NMR) signals from $CH_3O(CH_2)_2CH_3$, $CH_3O(CH_2)_3Cl$ and A. The values of differences between the chemical shift of corresponding signals for A and for the free ether $CH_3O(CH_2)_2CH_3$ are also given, as $\Delta = \delta(A) - \delta(\text{ether})$. These differences in chemical shift are in agreement with those observed for the zinc analogue [4], for which the shift in the β proton resonances is in the opposite direction to that for all other protons. The coupling constants $^{2}J(^{1}H_{\alpha}-^{113}Cd)$ and $^{3}J(^{1}H_{\beta}-^{113}Cd)$ are 52.32 Hz and 63.00 Hz respectively. There is no sign of any coupling of the ^{113}Cd nucleus to the γ or δ protons.

A comparison of the ^{13}C NMR spectrum of A with that of the ether $CH_3O(CH_2)_2CH_3$ (Table 2) is informative. It is generally accepted that a shift to high field (shielding) of the γ-C atom of a complex with respect to the γ-C atom of the free ligand, in this case the ether ($\Delta\delta(A) - \delta(\text{ether})$), is evidence for the formation of a five- or six-membered ring system [12]. Such a shift, albeit very small ($\Delta = -1.03$ ppm), was seen when the spectrum of the zinc-containing analogue of A was compared with that of the free ether [4] and was taken as crucial evidence that there was internal coordination of O to Zn in the organometallic compound. As can be seen from the data given in Table 2, there is no such effect for A; indeed a downfield (deshielded)

TABLE 2. Positions of resonances seen in the ^{13}C nuclear magnetic resonance spectra of $CH_3O(CH_2)_2CH_3$ and $(CH_3O(CH_2)_3)_2Cd$ (A)

$CH_3O(CH_2)_2CH_3$ δ(ether) (ppm)	$(CH_3O(CH_2)_3)_2Cd$ δ(A) (ppm)	$\Delta = \delta(A) - \delta(\text{ether})$ (ppm)
9.46 (α)	11.72 (α)	+2.26
22.03 (β)	29.28 (β)	+7.25
73.22 (γ)	76.14 (γ)	+2.92
56.90 (δ)	58.22 (δ)	+1.32

shift of +2.92 ppm is seen for this atom, a value similar to that seen for many dialkyl-zinc and dialkyl-cadmium compounds for which there cannot be any internal coordination. For example, the difference between the ^{13}C shift; for the γ-C atoms of $(CH_3(CH_2)_3)_2Zn$ and $CH_3(CH_2)_2CH_3$ ~ +4.83 ppm. Thus it appears that there is no internal coordination of O to Cd in **A**.

Although the proton-coupled ^{113}Cd NMR spectrum of **A** appears to be extremely complex, it can be simulated by using the coupling constants of the ^{113}Cd nucleus to the α and β protons obtained from the ^{1}H NMR spectrum of **A**.

3.4 Formation of an adduct between A and 2,2′-bipyridyl

Condensation of liquid **A** onto a small amount of solid 2,2′-bipyridyl afforded a crystalline orange compound, thought to be the adduct $(CH_3O(CH_2)_3)_2Cd \cdot$ 2,2′-bipyridyl (**B**). That behaviour was observed for the zinc analogue of **A**. It was found that **B** was extremely thermally sensitive; thus it dissociated into its constituents when warmed to temperatures as low as 30°C. Because of this extreme thermal sensitivity it was impossible to grow crystals suitable for a single-crystal X-ray diffraction study.

Two significant items of spectroscopic data were obtained for **B**. First it was found that λ_{max} for a solution of **B** in *n*-hexane, is at 360 nm. Thus **B** absorbs at a similar wavelength to the bipyridyl adduct of $(CH_3)_2Cd$ (where $\lambda_{max} \approx 350$ nm) [11]. By comparison with the zinc analogues of these compounds it would be expected that, if the O atoms in **A** were intramolecularly coordinated to the Cd atom, then λ_{max} for **B** would be at a longer wavelength than λ_{max} for the corresponding 2,2′-bipyridyl adduct of $(CH_3)_2Cd$. Such a difference in λ_{max} was seen between the 2,2′-bipyridyl adducts of $((CH_3)_2N(CH_2)_3)_2Zn$ and $(CH_3)_2Zn$ [4].

Secondly the ^{13}C NMR spectrum was determined. It has been reported that a comparison of the ^{13}C NMR chemical shift of the resonance of the C(1) atoms of a 2,2′-bipyridyl adduct with that for uncoordinated 2,2′-bipyridyl can give an indication of the strength of binding of the bipyridyl unit to the metal atom [4]. The closer the two values are to each other, the weaker the binding. The value of 156.61 ppm that we observe (cf. for the **B** value of 156.52 ppm for free 2,2′-bipyridyl) is indicative of very weak coordination.

4. Conclusions

It is clear from the data presented that a novel compound $(CH_3O(CH_2)_3)_2Cd$ (**A**) has been prepared. The spectroscopic results discussed above provide a body of evidence to show that internal co-ordination does not occur in **A**. It is perhaps not surprising to find that internal coordination occurs from O to Zn, but not from O to Cd in view of the lower tendency of cadmium to form coordinate bonds with less polarizable "A-type" donor atoms.

Compound **A** appears to have little advantage over more conventional cadmium sources for CdS or CdSe production by MOCVD. Even though it is quite thermally stable, its low volatility would disfavour its use as a precursor in such processes.

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