Journal of Organometallic Chemistry, 421 (1991) 129–136
Elsevier Sequoia S.A., Lausanne
JOM 22193

The adduct formed between dimethylcadmium and 1,4-dioxane, 1,4-dioxanedimethylcadmium(II): a crystallographic and spectroscopic study

Matthew J. Almond, Michael P. Beer, Michael G.B. Drew and David A. Rice *
Department of Chemistry, University of Reading, Whiteknights, Reading, Berkshire, RG6 2AD (UK)

(Received June 27th, 1991)

Abstract

The reaction of dimethylcadmium with 1,4-dioxane gives a 1:1 adduct, 1. Recently it has been shown that the growth of CdS by metal organic chemical vapour deposition (MOCVD) is improved if the commonly used dimethylcadmium is replaced by 1. The nature of 1 in the solid state was unknown and so a sample of 1 was sublimed *in vacuo* to give colourless crystals, on which an X-ray diffraction study was carried out. The cadmium atom is four coordinate, being bound to two methyl groups (Cd–C 2.09(2) Å) and two oxygen atoms (Cd–O(1) 2.88(2) Å, Cd–O(4*) 2.75(2) Å) from different 1,4-dioxane molecules, giving rise to an unusual one-dimensional polymeric structure. Evidence for an association between dimethylcadmium and 1,4-dioxane in benzene solution was obtained from a spectroscopic study. 1 is not transported in the gas-phase in sizeable quantities, thus casting doubt upon the role conventionally assigned to it in reducing side reactions in MOCVD.

Introduction

Adducts of dimethylcadmium are currently under investigation for use as volatile precursors in the MOCVD production of the semiconductor cadmium sulphide [1]. The growth of this material on to substrates of gallium arsenide from pure dimethylcadmium and hydrogen sulphide suffers from prereaction [2], i.e. a premature reaction of the precursors before the heated substrate is reached. The problem is reduced, but not eliminated, by replacing the pure dimethylcadmium in the reaction with 1. The mechanism by which the adduct reduces the problem of prereaction is unknown and is at present under debate. It has been said that the adduct is transported in the gas phase, thus reducing the ease with which CdS is formed, while others have failed to observe such adducts in the gas phase [3].

We have been addressing the problem of prereaction in CdS formation by MOCVD. Our research was hindered by the lack of structural information available for species such as 1, the only other dimethylcadmium adduct to have been studied is that with 2,2'-bipyridyl [4]. It has been suggested [5], that in the solid state, 1 consists of monomeric molecules with the 1,4-dioxane ligand chelating to the cadmium centre. This suggestion is in agreement with the observation that most four coordinate cadmium(II) species are monomeric [6] but we felt that the existence of chelating 1,4-dioxane in the solid state was unlikely. To aid our investigation into the prereaction in CdS formation we therefore decided to determine the structure in the solid state of **1**.

Experimental

Preparative methods

The reactants and solvents used were rigorously dried before use as was all the glassware used in the preparations. The adduct was prepared on an all glass vacuum line.

Dimethylcadmium was prepared by the reaction of anhydrous $CdCl_2$ (98.2 g, 0.54 mol) with MeMgI (which was synthesised from magnesium turnings (30.0 g, 1.23 mol) and methyl iodide (180.0 g, 1.23 mol)) following published procedures [7] to yield an ethereal solution of dimethylcadmium. The bulk of the solvent, ca. 90%, was removed by distillation at atmospheric pressure. The remaining products were allowed to cool under nitrogen. The flask, containing the desired product, was transferred to a vacuum line and the product distilled under a dynamic vacuum on to 83.7 g (0.54 mol) of dry and vacuum-sublimed 2,2'-bipyridyl. The adduct thus formed was isolated and cracked following published procedures [8] to give a sample of pure dimethylcadmium.

A sample of **1** was prepared by distilling 1,4-dioxane on to an equimolar amount of dimethylcadmium on a vacuum line. Vacuum sublimation of the resulting colourless crystalline solid produced the crystals used in this study.

Crystal structure determination

A crystal of **1**, formed as previously described, was selected for study. Crystal data for **1**, $[CdC_6O_2H_{14}]$, $M = 230.5$, orthorhombic, $a = 4.284(4)$, $b = 14.770(12)$, $c = 13.170(11)$ Å, $V = 833.3$ Å^3, $F(000) = 456$, $D_{calc} = 1.84$ g cm^{-3}, $Z = 4$, Mo-K_α radiation ($\lambda = 0.7107$ Å), μ(Mo-K_α) = 25.4 cm^{-1}, space group *Pbcm*, $T = 298$ K, zirconium-filtered radiation.

A crystal of approximate size 0.3 × 0.3 × 0.3 mm^3 was mounted in a capillary tube under nitrogen. Preliminary examination to assess crystal quality and establish the space group was carried out on a precession camera. The crystal was then mounted upon a STOE-2 diffractometer to rotate around the *a* axis. A total of 721 independent reflections were measured with a 2θ minimum of 50° (0 to $+h$, 0 to $+k$, 0 to $+l$). Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. No decay in intensity was observed for the standard reflections. In subsequent calculations 483 reflections with $I > 2\sigma(I)$ were used. The position of the cadmium atom was determined from the Patterson function. The position of the remaining atoms in the molecule were located by successive cycles of difference Fourier syntheses and least-squares refinements. An empirical absorption correction was applied [9] (maximum 1.80, minimum 0.52). All non-hydrogen atoms in the molecule were given anisotropic thermal parameters. Hydrogen atoms in the methylene groups were included in calculated positions. Those in the methyl group were observed in a difference Fourier map and refined independently apart from C–H bond length constraints.

Table 1

Atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Cd	9415(4)	6227(2)	2500
O(1)	5587(35)	7833(12)	2500
C(2)	4332(59)	8249(17)	1540(20)
C(3)	5160(28)	9210(14)	1660(11)
O(4)	3898(44)	9636(12)	2500
C(5)	9590(37)	6297(15)	917(17)

Calculations were performed using full-matrix least-squares methods with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. Calculations were performed using SHELX76 [10] and some of our own programs on the Amdahl 5870 Computer at the University of Reading. The final R value was 0.072 ($R_w = 0.079$). In the final cycle of refinement, no shift was $> 0.1\sigma$ and there were no significant peaks in the final difference Fourier map. Positional coordinates are given in Table 1 and dimensions around the metal atom are given in Table 2.

Spectroscopic study

Crystals of **1** were prepared as previously described and transferred to a nitrogen containing drybox, where they were ground using an agate pestle and mortar. A hexachlorobutadiene mull was prepared for infrared measurements with a Perkin–Elmer FTIR 1720-X interferometer.

For recording of the NMR spectra of **1** equimolar amounts of dimethylcadmium and 1,4-dioxane were condensed into an NMR tube attached to a vacuum line. On to the solid thus formed was condensed the minimum of dry benzene-d_6 required to give a solution. Proton and ^{13}C spectra were recorded with a Bruker WM 250 Fourier transform spectrometer at 250.13 and 62.89 MHz respectively. A JEOL FX 90Q Fourier transform spectrometer was used to record the ^{113}Cd spectrum (operating at 19.8 MHz) and those of free dimethylcadmium. All spectra were recorded at room temperature.

To obtain mass spectra, the vapour above **1** was examined with a Vacuum Generator's SXP800 quadrupole mass spectrometer.

Table 2

Molecular dimensions in the metal coordination sphere, distances (Å) and angles (deg) [a]

Cd–O(1)	2.884(17)
Cd–C(5)	2.089(23)
Cd–O(4*)	2.745(18)
O(1)–Cd–O(4*)	114.2(5)
O(1)–Cd–C(5)	88.8(6)
C(5)–Cd–O(4*)	93.5(6)
C(5)–Cd–C(5**)	173.0(8)

[a] * symmetry element $1-x$, $-1/2+y$, z; ** symmetry element x, y, $1/2-z$.

Results and discussion

The crystal structure of 1

The reaction of dimethylcadmium and 1,4-dioxane yields **1**, which does not have a molecular structure as previously suggested [5] but is polymeric in nature with 1,4-dioxane molecules acting as bridges between the metal centres. Thus the structure consists of linear polymeric chains of general formula $-Cd(Me)_2$ (dioxane)$-Cd(Me)_2$(dioxane)$-$. The polymeric nature of **1** is shown in Fig. 1 where the atom-numbering scheme is also given. Selected bond lengths and angles are given in Table 2. The cadmium atom and both of the oxygen atoms that are coordinated to the metal, are positioned on mirror planes in the *z* direction such that the polymeric chains sit astride mirror planes and are directed along the *y* direction.

Thus each cadmium atom is four coordinate, being bound to two carbon atoms from the methyl groups and two oxygen atoms from different 1,4-dioxane rings. The Cd–C distance (2.09(2) Å) in **1** is comparable to those found in $Me_2Cd \cdot 2,2'$-bipy [4] (2.172(25) Å, 2.152(22) Å). However, the Cd–O distances (Cd–O(1) 2.88(2), Cd–O(4*) 2.75(2) Å) are longer than that in $CdBr_2 \cdot 1,4$-dioxane (2.47(6) Å) [11], reflecting the difference in electronegativity between Br and the methyl group, with the former causing a greater Lewis acidity at the metal atom than the latter.

The geometry of the metal coordination sphere is very irregular with a near linear C–Cd–C moiety (C(5)–Cd–C(5**) 173.0(8)°) as well as an O(1)–Cd–O(4*) angle of 114.2(5)° and O(1)–Cd–C(5) and C(5)–Cd–O(4*) angles of 88.8(6) and 93.5(6)°, respectively. Perhaps the best description of the geometry around the metal is that of an approximate trigonal bipyramid with the methyl groups in axial positions and two of the equatorial sites occupied by oxygen atoms with the third site being vacant.

The angles subtended at the metal centre can be explained by assuming that the cadmium atom uses *sp* hybrids to bond the two methyl groups with the lone pairs from the two oxygen atoms being accepted into two cadmium orbitals that are predominately *p* in character. These latter two, if purely *p* in nature, would be at 90°, but the steric requirements of the chair shaped ligands cause an increase from 90 to 114.2(5)°.

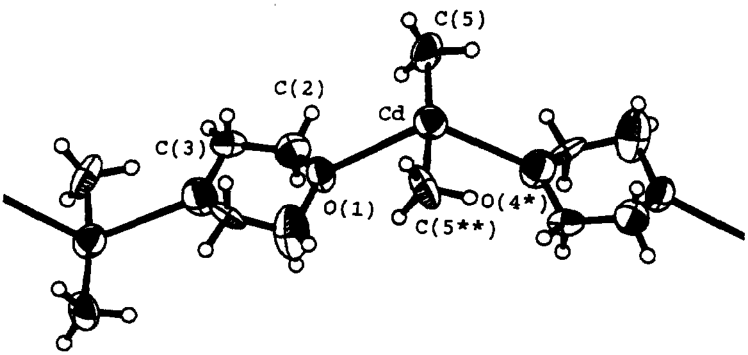

Fig. 1. ORTEP plot of 1,4-dioxanedimethylcadmium(II).

The 1,4-dioxane ring in **1** has a chair shape as indicated by the torsion angles around the ring, which are successively (starting from a O–C–C–O) -60.0, 64.0, -64.0, 60.0, -56.8, 56.8°. This shows that the ligand does not chelate as other authors have proposed [5]. Indeed the dimensions of the ring indicate that its coordination to Me_2Cd does not cause any significant change in the geometry of the ligand molecule compared with that found by a gas-phase electron diffraction study [12].

From the data provided by the crystal structure, indicating the presence of long Cd–O bonds and a polymeric nature, we conclude that it is very unlikely that heating **1** would result in the adduct being transported in the gas phase. Thus it is likely that decomposition occurs to the two constituent molecules that recombine on cool surfaces to form crystalline material.

Spectroscopic study

The role of the 1,4-dioxanedimethylcadmium(II) adduct in the MOCVD growth of CdS is unclear, especially in view of the conclusions drawn from the crystal structure that are given above. To further clarify the role of **1** in MOCVD its mass spectrum was measured.

The mass spectrum of **1** did not contain the parent ion peak, the highest mass peak having an m/e value of 215, which corresponds to the mass of **1** minus the mass of a methyl group. The intensity of this peak was just above detection limit. This result could be said to provide some evidence for the existence of the adduct in the gas phase although, at this stage, the possibility of an equilibrium in the gas phase between **1** and its components cannot be ruled out.

Frequencies of bands in the solid phase infrared spectrum of **1** are given in Table 3. Studies of gas phase samples of dimethylcadmium in this laboratory have indicated that the asymmetric C–Cd–C stretch exhibits P and R branches at 544 and 529 cm^{-1}, respectively, whilst in the Raman spectrum the symmetric stretch appears at 473 cm^{-1} [13]. In the infrared spectrum of **1** we observe one band in this region at 490 cm^{-1}, which upon comparison with the results obtained from our study of the 2,2'-bipyridyldimethylcadmium(II) adduct [4] we assign to the asymmetric C–Cd–C mode in the adduct molecule. The observed drop in the metal–carbon stretching frequency on the formation of a coordination complex is in accord with our previous findings. A symmetric C–Cd–C stretch is not expected in the infrared spectrum because of the near linear structure of the fragment. The observation that the bands of the 1,4-dioxane moiety are largely unshifted upon adduct formation is indicative of absence of perturbation in the moiety upon coordination. An infrared spectrum of gaseous **1**, measured at 50 ° C, showed no evidence for the existence of the adduct in the gas phase. The spectrum was that to be expected of a mixture of gaseous Me_2Cd and 1,4-dioxane. This result is entirely consistent with reported studies [3].

The ^{113}Cd, ^{13}C and ^{1}H NMR spectra of **1**, 1,4-dioxane and dimethylcadmium were recorded in benzene-d_6 solutions. The observed shifts are listed in Table 4. The results indicate that dimethylcadmium and 1,4-dioxane are associated in solution; however, the degree of association cannot be determined. It may be that time-averaged spectra were measured. Unfortunately, the lack of facilities for variable temperature measurements precluded further investigation. Comparison of the ^{1}H spectra of **1** and dimethylcadmium reveals that the methyl protons are

Table 3

Frequencies of bands in the infrared spectrum of 1

Frequencies [a] ν (cm^{-1})	Approximate description [b]
490m	ν_{as}(C–Cd–C) (DMCd)
614m	ring bend
675m	$\delta(CH_3)$(DMCd)
878s	ring stretch
889m	CH_2 rock
1026m	
1050wm	ring stretch
1085m	CH_2 rock
1125s	ring stretch
1255s	CH_2 twist
1290m	CH_2 twist
1325w	
1367wm	CH_2 wag
1425wm	
1455m	CH_2 scissor
1956w	
1983w	
2693w	
2756w	
2789wm	
2805wm	CH_2 stretches
2854ms	
2888m	
2915ms	ν(CH) (DMCd)
2961ms	CH_2 stretches

[a] Sample prepared as hexachlorobutadiene mull. Letters are a measure of relative intensity: w = weak, m = medium, s = strong. [b] Fundamentals of vibrations of the 1,4-dioxane fragment assigned using ref. 14.

Table 4

^1H, ^{13}C and ^{113}Cd NMR data[a,b] for dimethylcadmium, 1,4-dioxane and 1,4-dioxanedimethylcadmium(II)

	Dimethylcadmium	1,4-Dioxane	1,4-Dioxanedimethylcadmium(II)
^1H	−0.56		−0.51
	(^2J(Cd–H) 50.00 Hz) [c]		($^2J(^{111}Cd–H)$ 49.21, $^2J(^{113}Cd–H)$ 51.33 Hz)
		3.43	3.34
^{13}C	−2.5		−3.4
	($J(^{13}C–Cd)$ 512.6, 536.4 Hz) [d]		($J(^{13}C–Cd)$ 521.9, 546.0 Hz) [d]
		67.0	67.0
^{113}Cd	545.0		535.0
	($^2J(^{113}Cd–H)$ 51.1 Hz) [e]		($^2J(^{113}Cd–H)$ 51.3 Hz) [e]

[a] ^1H and ^{13}C spectra (δ(ppm)) referenced to $(CH_3)_4Si$. ^{113}Cd spectra obtained on a 90 MHz spectrometer operating at 19.83 MHz with 45.20 kHz offset equal to 0 ppm. [b] All spectra recorded at 298 K. [c] Broad coupling peak due to superposition of ^{113}Cd and ^{111}Cd coupling peaks. This spectrum was measured with JEOL FX 90Q Fourier transform spectrometer. [d] These couplings arise from the influence of the ^{111}Cd and ^{113}Cd nuclei. [e] ^1H coupling gives septet.

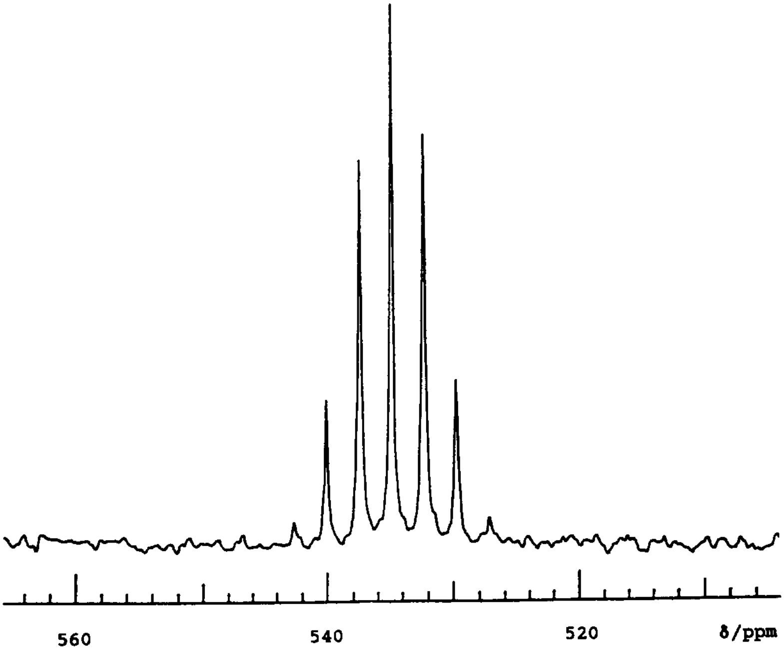

Fig. 2. ^1H–^{113}Cd NMR spectrum of 1,4-dioxanedimethylcadmium(II).

deshielded by +0.05 ppm upon adduct formation. This is in accord with the results that we obtained for the 2,2'-bipyridyldimethylcadmium(II) adduct, also measured in C_6D_6 solution, although the shift is somewhat smaller. This is again an indication of the small effect that adduct formation has on each of the constituents of the adduct. The methyl resonance shift in the ^{13}C spectrum is indicative of an increase in shielding (−0.9 ppm) upon adduct formation. Again the direction of the shift is in accord with our previous study, but again, the shift is smaller.

The ^1H–^{113}Cd spectrum of **1** (Fig. 2) has the expected septet structure with ^2J(Cd–H) 51.3 Hz (51.1 Hz in dimethylcadmium). The peaks observed are sharp, indicating that there is no further significant coupling to ligand protons. The detection of sharp ^1H–^{113}Cd coupling in **1** was particularly interesting since in $Me_2Cd \cdot$ 2,2'-bipy [4] the comparable peaks were broadened as a result of the influence exerted by the protons of the aromatic bipyridyl rings.

Conclusions

1 has been shown to be polymeric in the solid state. It is not transported, at least in sizeable amounts, in the gas phase. Therefore the role played by **1** in reducing the prereaction in the MOCVD formation of CdS is not attributable to the presence of an adduct in the gas phase. It is possible that free 1,4-dioxane plays a role in reducing surface reactions that are known to bedevil the chemistry of gaseous dimethylcadmium, and this aspect is being investigated.

Acknowledgement

We acknowledge the contributions of Mr. A. Jahans who assisted with the collection of the X-ray data, and of Mr. P. Heath and Mr. G. Thompson who recorded the NMR spectra.

We thank the SERC and RSRE, Malvern U.K. for support and for providing a CASE award (M.P.B.).

References

1 A.C. Jones, S.A. Rushworth, P.J. Wright, B. Cockayne, P. O'Brien and J.R. Walsh, J. Cryst. Growth, 97 (1989) 537.
2 P.J. Wright, B. Cockayne, A.C. Jones, E.D. Orrell, P. O'Brien and O.F.Z. Khan, J. Cryst. Growth, 94 (1989) 97.
3 O.F.Z. Khan, P. O'Brien, P.A. Hamilton, J.R. Walsh and A.C. Jones, Chemtronics, 4 (1989) 244.
4 M.J. Almond, M.P. Beer, M.G.B. Drew and D.A. Rice, Organometallics, 10 (1991) 2072.
5 K.H. Thiele, Z. Anorg. Allg. Chem., 330 (1964) 8.
6 F.H. Allen, O. Kennard and R. Taylor, Cambridge Structural Database, Acc. Chem. Res., 16 (1983) 146.
7 E. Krause, Ber. Dtsch. Chem. Ges., 50 (1917) 1813.
8 D.V. Shenai-Khatkhate, E.D. Orrell, J.B. Mullin, D.C. Cupertino and D.J. Cole-Hamilton, J. Cryst. Growth, 77 (1986) 27.
9 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 39 (1983) 158.
10 G.M. Sheldrick, SHELX76, Package for Crystal Structure Determination, University of Cambridge, 1976.
11 J.C. Barnes and L.J. Sesay, Inorg. Nucl. Chem. Lett., 13 (1977) 153.
12 M. Davis and O. Hassel, Acta Chem. Scand., 17 (1963) 1181.
13 I.S. Butler and M.L. Newbury, Spectrochim. Acta, 33A (1977) 669.
14 O.H. Ellestad, P. Klaboe and G. Hagen, Spectrochim. Acta, 27A (1971) 1025.