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The Adduct Formed between Dimethylcadmium and 2,2′-Bipyridyl, (2,2′-Bipyridyl)dimethylcadmium(II): 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 RG6 2AD, U.K.

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Summary: The reaction of dimethylcadmium with 2,2′-bipyridyl gives a 1:1 adduct (**1**). By heating **1**, followed by trap to trap distillation of the evolved liquid, pure dimethylcadmium can be obtained. This process is more efficient than repeated vacuum distillation of crude dimethylcadmium obtained directly from a Grignard reaction. A sample of **1** was recrystallized by sublimation in vacuo to give yellow crystals whose structure has been determined. The crystals are orthorhombic and of space group *Pbca* with $Z = 8$, $a = 15.710$ (11) Å, $b = 11.784$ (12) Å, and $c = 13.540$ (10) Å. A total of 1038 reflections above background were collected on a diffractometer, and the structure was solved by the heavy-atom method. The cadmium atom is four-coordinate, being bound to two methyl groups [Cd–C(13) 2.172 (25) Å, Cd–C(14) 2.152 (22) Å] and two nitrogen atoms [Cd–N(1) 2.503 (13) Å, Cd–N(8) 2.535 (14) Å] from a chelating 2,2′-bipyridyl molecule. The C(13)–Cd–C(14) angle [148.4 (8)°] is larger than expected for an angle at a tetrahedral center, while a small "bite" angle [N(1)–Cd–N(8) 64.0 (5)°] is subtended by the ligand. The angle between the C(13)–Cd–C(14) and N(1)–Cd–N(8) planes is 79.0°, and there are no inter- or intramolecular contacts that can be said to cause the deviation from the regular value of 90°. Evidence for the existence of **1** not only as a solid but also as a vapor and in benzene and diethyl ether solutions was obtained from a spectroscopic study.

We are currently investigating methods of producing pure dimethylcadmium, which is needed to prepare, via metal organic vapor-phase epitaxy [MOVPE], a variety of II–VI devices including the infrared detector, $Cd_xHg_{1-x}Te$, as epitaxial layers on crystalline gallium arsenide.[1]

Dimethylcadmium is usually prepared from the reaction of methyl magnesium iodide with cadmium chloride. Unfortunately, it is difficult to free the product from residual traces of the solvent (an ether) and/or methyl iodide. One method of producing pure metal alkyls is to make from them solid coordination compounds, which are pumped free of solvent and impurities.[2] The adducts are heated in vacuo to release pure samples of the metal alkyl. Exploitation of this method to make pure dimethylcadmium is hampered because, although adducts of dimethylcadmium were studied in the 1960s, there is little published information on them.

Recently, the adduct of dimethylcadmium with 2,2′-bipyridyl, 1, has received much attention as a possible source of pure dimethylcadmium.[2] It is claimed that pure dimethylcadmium is obtained by dissociation of the adduct on warming to ca. 70 °C, while in contrast, other workers have stated that 1 dissociates fully at ambient temperature,[3] thus preventing growth of crystals of 1.

Because of the important role proposed for 1 in obtaining pure dimethylcadmium and the uncertainty concerning its dissociation, we felt it important to ascertain the structure and spectroscopic properties of the species and also to examine its vapor transport. Does the adduct sublime undissociated? If so, it is possible that some samples of so-called "pure" dimethylcadmium obtained from this adduct may be contaminated by traces of 2,2′-bipyridyl. A considerable impetus was also given to our research by the lack of structural data on species such as 1. We have succeeded in growing single crystals of 1 in vacuo, and we present a report of the first X-ray diffraction study of a compound containing dimethylcadmium.

Experimental Section

Preparative Methods. The solvents and reactants were rigorously dried before use as was all the glassware used in the preparations. The adduct was isolated and decomposed by using an all-glass vacuum line.

Dimethylcadmium was prepared from the reaction of anhydrous $CdCl_2$ (98.2 g, 0.54 mol) with MeMgI [which was synthesized from Mg turnings (30.0 g, 1.23 mol) and methyl iodide (180.0 g, 1.23 mol)] following published procedures[4] to give 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 onto 83.7 g (0.54 mol) of dry and vacuum-sublimed 2,2′-bypyridyl. A bright yellow solid was formed. The mixture of the adduct and excess of unreacted ligand were kept at room temperature and pumped under dynamic vacuum for 2 h in order to remove the most volatile impurities. The resulting solid mixture was heated to 70 °C in a static vacuum, under which conditions decomposition took place, and the volatile dimethylcadmium so liberated was trapped in an adjacent vessel kept at liquid nitrogen temperature. During the period in which the dimethylcadmium was evolved, crystals of the adduct 1 formed on the cooler parts of the vacuum line. These were subsequently transferred to an oxygen-free, nitrogen-containing drybox.

The dimethylcadmium obtained directly by heating 1 was found to contain some diethyl ether. The impure material was allowed to vacuum distill on an all-glass apparatus fitted with greaseless taps. The dimethylcadmium/diethyl ether sample was held at 2 °C and was allowed to distill successively into two traps, the first being held at −30 °C, and the second at −196 °C. Pure dimethylcadmium collected in the trap at −30 °C, while the ether was isolated at −196 °C.

Crystal Structure Determination. A crystal of 1, formed during the procedure used to purify dimethylcadmium (see Preparative Methods), was selected for study.

Crystal Data: $CdMe_2(bpy)$, $CdC_{12}N_2H_{14}$, orthorhombic, $F(000) = 1184$, $M = 298.5$, $a = 15.710$ (11) Å, $b = 11.784$ (12) Å, $c = 13.540$ (10) Å, $V = 2506.6$ Å^3, $D_{calcd} = 1.58$ g cm^{-3}, $Z = 8$, $\lambda = 0.7107$ Å, μ(Mo Kα) = 17.02 cm^{-1}, spacegroup *Pbca*, $T = 298$ K, zirconium-filtered radiation.

A crystal of approximate size 0.3 × 0.3 × 0.3 mm^3 was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer, and data were collected via variable width ω scan. Background counts were for 20 s, and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. A total of 2363 independent reflections

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Table I. Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Cd	2203 (1)	3765 (2)	6338 (1)
N(1)	882 (9)	4671 (11)	7007 (10)
C(2)	937 (19)	5336 (18)	7853 (15)
C(3)	243 (20)	5692 (24)	8354 (20)
C(4)	−532 (19)	5493 (22)	7942 (20)
C(5)	−577 (12)	4810 (19)	7082 (15)
C(6)	137 (9)	4400 (16)	6648 (12)
C(7)	87 (9)	3741 (16)	5805 (13)
N(8)	821 (9)	3215 (13)	5498 (12)
C(9)	846 (11)	2602 (17)	4709 (16)
C(10)	132 (15)	2388 (22)	4151 (19)
C(11)	−581 (16)	2875 (22)	4410 (16)
C(12)	−635 (11)	3558 (17)	5211 (16)
C(13)	2469 (12)	2598 (29)	7541 (21)
C(14)	2683 (15)	4831 (27)	5174 (17)

Table II. Molecular Dimensions in the Coordination Sphere

Distances (Å)			
Cd–N(1)	2.503 (13)	Cd–C(13)	2.172 (25)
Cd–N(8)	2.535 (14)	Cd–C(14)	2.152 (22)
Angles (deg)			
N(1)–Cd–N(8)	64.0 (5)	N(1)–Cd–C(14)	107.8 (8)
N(1)–Cd–C(13)	99.1 (7)	N(8)–Cd–C(14)	96.9 (7)
N(8)–Cd–C(13)	109.9 (8)	C(13)–Cd–C(14)	148.4 (8)

were measured (with $2\theta < 50°$; 0 to $+h$, 0 to $+k$, 0 to $+l$), of which 1038 with $I > 2\sigma(I)$ were used in subsequent refinement. No deterioration in the crystal was observed during the data collection. The absorption correction ranges between 0.70 and 1.64.[5] The structure was determined by the heavy-atom method. Hydrogen atoms were included in calculated positions, although the methyl hydrogen atoms were refined as rigid groups. All non-hydrogen atoms were given anisotropic thermal parameters. Data were given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.087 ($R_w = 0.095$).

Calculations were carried out by using Shelx76[6] and some of our own programs on the Amdahl 5870 computer at the University of Reading. In the final cycles of refinement, no shift/error ratio was greater than 0.1σ. In the final difference Fourier maps, the maximum and minimum peaks were 1.02 e Å^{-3} (located close to the metal atom) and −0.97 e Å^{-3}. Positional parameters are given in Table I and selected molecular dimensions in Table II. Supplementary material includes anisotropic thermal parameters, hydrogen atom positions, and structure factor tables.

Spectroscopic Study. Crystals of 1, taken from the same preparation as the one used for the structural study, were ground with an agate pestle and mortar in a drybox, and mulls [hexachlorobutadiene (hcb)] were prepared for infrared spectroscopic measurements (4000–220 cm^{-1}) using a Perkin-Elmer FTIR 1720-X interferometer.

In a drybox further crystals of 1, ca. 5 mg, from the same preparation, were placed into a 1-cm silica UV–visible cell. The cell was quickly filled with sodium-dried diethyl ether, 3 mL, and stoppered. The UV–visible spectrum (900–200 nm) was recorded by using a Kontron Uvikon 860 spectrometer.

To obtain a Raman spectrum of 1 a dry sample of 2,2′-bipyridyl was placed in a 5 mm diameter NMR tube attached to the vacuum line. After the tube was evacuated, an excess of dimethylcadmium was distilled onto the solid to produce the adduct. The excess of dimethylcadmium was removed in vacuo and the tube sealed. The Raman spectrum was obtained by the FT-IR Raman technique[7] (300–3500 cm^{-1}) using a modified Perkin-Elmer 1710 interferometer at the University of Southampton.

A further sample of 1 was prepared in an NMR tube in a similar manner to that used for the Raman studies. Onto it was distilled the minimum of dry benzene-d_6 required to form a solution. Proton, ^{13}C, and ^{113}Cd NMR spectra were recorded at room temperature with a JEOL FX 90Q Fourier transform spectrometer at 88.6, 22.5, and 19.8 MHz, respectively.

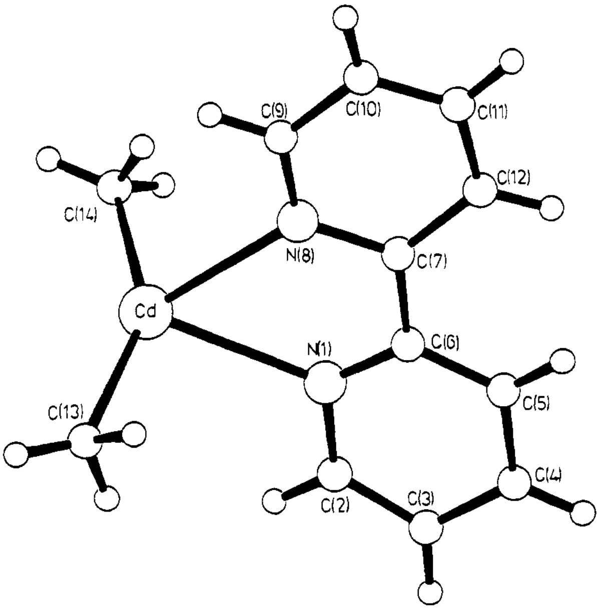

Figure 1. Crystal structure of 1.

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

Results and Discussion

(a) Crystal Structure of (2,2′-Bipyridyl)dimethylcadmium(II). The reaction of dimethylcadmium and 2,2′-bipyridyl yields the molecular species 1, which is depicted in Figure 1, where the atom-numbering scheme is also given. Selected bond lengths and angles are given in Table II.

The cadmium atom is four-coordinate, being bound to two carbon atoms from the methyl groups [Cd–C(13) 2.172 (25) Å, Cd–C(14) 2.152 (22) Å] and two nitrogen atoms [Cd–N(1) 2.503 (13) Å, Cd–N(8) 2.535 (14) Å] from a chelating 2,2′-bipyridyl molecule. The observed molecular structure is similar to that reported for the adduct (2,2′-bipyridyl)bis((trimethylsilyl)methyl)cadmium (2)[3] [Cd–C 2.19 (6) and 2.09 (5) Å; Cd–N 2.53 (3) and 2.52 (4) Å]. Bushnell and Stobart also report that the adduct of dimethylcadmium and 2,2′-bipyridyl, which forms the subject of the present study, dissociates completely at ambient temperature.

Although the cadmium atom in 1 is four-coordinate, the angles subtended at it are far from those expected at a tetrahedral center. The C(13)–Cd–C(14) angle [148.4 (8)°] is surprisingly large although the related angle in 2 is 156 (2)°. The large angle in 2 could be ascribed to the steric requirements of the bulky $(CH_3)_3SiCH_2$ groups, but such requirements cannot pertain in the present structure. Photoelectron spectra of dimethylmercury[8] and ESR measurements on the dimethylmercury cation[9] suggest that there is little sp hybridization of the metal orbitals in dimethylmercury and that the lowest lying σ carbon–metal molecular orbital is formed by the s orbital on the metal, with the other being of p_z character. If, as is likely, a directly related system persists in 1 and 2, the C–Cd–C

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angle would be expected to be 180°, with the p_y and p_x orbitals on the metal, which of course are at 90° to each other, being available for bonding to the ligand. However, the "bite" angle of the ligand is expected, because of constraints imposed by the ligand, to be less than 90° and in 1 it is 64.0 (5)° [65 (1)° in 2]. It is highly probable that the cadmium-carbon bonding in coordinated dimethylcadmium is similar to that in the free metal alkyl, thus accounting for the large C–Cd–C angle and indicating that there is little sp hybridization. Examination of the published single-crystal X-ray data on 1,10-phenanthroline and 2,2′-bipyridyl complexes of the type $MX_2 \cdot L$ (L = 1,10-phenanthroline, 2,2′-bipyridyl; M = Zn, Cd, Hg; X = halide or alkyl) in which the metal center is in a nonplanar four-coordinate environment indicates that the C–Cd–C angles observed in 1 and 2 are unusually large compared to the normal MX_2 angles. Larger angles are observed for some related mercury alkyl species (range 164–168°[10]), while those of the comparable dichloro zinc species are smaller (range 114–117°[11]). This is in accord with the bonding model discussed above, i.e. cadmium and mercury forming σ metal–carbon bonds in which little or no sp hybridization occurs. It is to be expected that zinc would exhibit a greater propensity to form hybrid orbitals.

The angle between the plane formed by the metal atom and the methyl carbon atoms [Cd–C(13)–C(14)] and that of the metal atom and the two nitrogen atoms [Cd–N(1)–N(8)] is 79.0°, while the related angle in 2 is 79.5°. The observed value in 1 differs from the 90° required by a tetrahedron, but there are no inter- or intramolecular interactions that can been said to cause the difference.

The dimensions of the coordinated 2,2′-bipyridyl in 1 are in accord with those reported previously as is the angle of 11.1° between the two planes of the two C_5H_4N rings of the ligand.[12]

(b) Spectroscopic Study. Whether adducts of dimethylcadmium exist in the gas phase is a matter of dispute and current interest. The crystals for the structure determination were grown via vacuum sublimation, and so it was relevant to ascertain by mass spectrometry if the adduct was transported as a molecular species. Although the mass spectrum obtained from the adduct did not contain a parent ion peak of 1, the highest mass peak was at m/e = 284. This values corresponds to the mass of 1 minus the mass of a methyl group and so provides strong evidence that the adduct does exist in the gas phase. Naturally, we cannot state if there is, in the gas phase, an equilibrium between the adduct and its constituents, namely dimethylcadmium and 2,2′-bipyridyl.

The infrared and Raman spectra of 1 in the region 3300–400 cm^{-1} (Table III) are in accord with those reported for many 2,2′-bipyridyl complexes.[13] We have reexamined the infrared spectrum of gaseous linear dimethylcadmium and find that the asymmetric C–Cd–C stretch exhibits P and R branches at 544 and 529 cm^{-1}, respectively, while in the Raman spectrum the symmetric stretch is reported at 473 cm^{-1}.[14] In the infrared spectrum of 1 (Figure 2a), we find one band in this region at 462 cm^{-1}, which is close in frequency to the symmetric C–Cd–C stretching mode shown by gaseous dimethylcadmium. However, in the Raman spectrum of 1 (Figure 2b), two bands were detected at 461 and 440 cm^{-1}, which can only be assigned to the two C–Cd–C stretching modes and thus we attribute the former to the asymmetric mode and the latter to the symmetric mode. The observed size of the drop in metal–carbon stretching frequency on the formation of a coordination complex is in accord with previous work.[15] The failure to detect the symmetric C–Cd–C stretch in the infrared spectrum of 1 is perhaps attributable to the large C–Cd–C angle, which in turn results in a small dipole change with the symmetric mode.

Table III. Frequencies of Bands in the Infrared and Raman Spectra of 1 (cm^{-1})

infrared (hcb mull)^d	Raman (solid)^d	approx descripn^{c,e}
b	440 (100‰)	ν_{sym} (C–Cd–C)
462 (m)	461 (54)	ν_{as}(C–Cd–C)
621 (m)	619 (14)	op ring
642 (m)		ip ring
737 (m)		δ(CH_3) DMCd
757 (s)		op δ(CH)
766 (ms)	764 (15)	ip ring
a	809 (6)	op δ(CH)
1011 (ms)	1004 (46)	ring breathing
1042 (m)		ip ring
1060 (w)	1058 (15)	ν(ring–ring)
1065 (w)		ip ring
1091 (m)		δ(CH)
1100 (w, sh)	1109 (31)	ip ring
b	1130 (14, sh)	ip ring
1149 (wm)	1153 (5, sh)	ip ring
1159 (m, sh)		ip ring
1250 (wm, sh)		ip ring
1256 (m)	1254 (10)	ip ring
1262 (wm, sh)	1277 (16)	ip ring
1306 (w, sh)	1304 (35)	δ(CH)
1316 (m)		δ(CH) DMCd
1347 (w)		δ(CH) DMCd
1420 (ms)		δ(CH)
1428 (wm, sh)	1427 (5)	δ(CH)
1441 (s)		δ(CH)
1457 (s)		δ(CH)
1476 (m)		δ(CH)
1489 (m)	1483 (24)	δ(CH)
1576 (w, sh)	1566 (11)	ip ring
1583 (s)	1586 (50)	ip ring
1593 (ms)		
1600 (ms, sh)		
2827 (m)	2819 (4)	ν(CH) DMCd
2905 (m)	2894 (10)	ν(CH) DMCd
2929 (vw)		ν(CH) DMCd
2956 (m)	2940 (3)	ν(CH) DMCd
3009 (wm)		ν(CH) DMCd
3041 (w)		ν(CH)
3058 (m, sh)	3064 (8)	ν(CH)
3069 (m)	3079 (6)	ν(CH)
3100 (w)		ν(CH)

[a] Absorption obscured by an intense absorption of hcb. [b] Absorption too weak to be observed. [c] See refs 14 and 17. [d] Figures and letters in parentheses denote the relative intensities of the spectral features. [e] Descriptions marked DMCd apply to the dimethylcadmium fragment; all others to the bipyridyl fragment; ip ring and op ring are used to describe in-plane and out-of-plane ring modes.

A recent development of MOVPE is the use of photolysis to induce epitaxial deposition. Many of the compounds that are used for thermal MOVPE do not possess the desired absorptions in the UV-visible region; thus methods of modifying the spectra of these compounds are being sought. Accordingly, we examined the UV-visible spectrum of 1. The only feature significantly different from those in the spectra of the two constituent parts is a shoulder on the long-wavelength flank of the 278-nm

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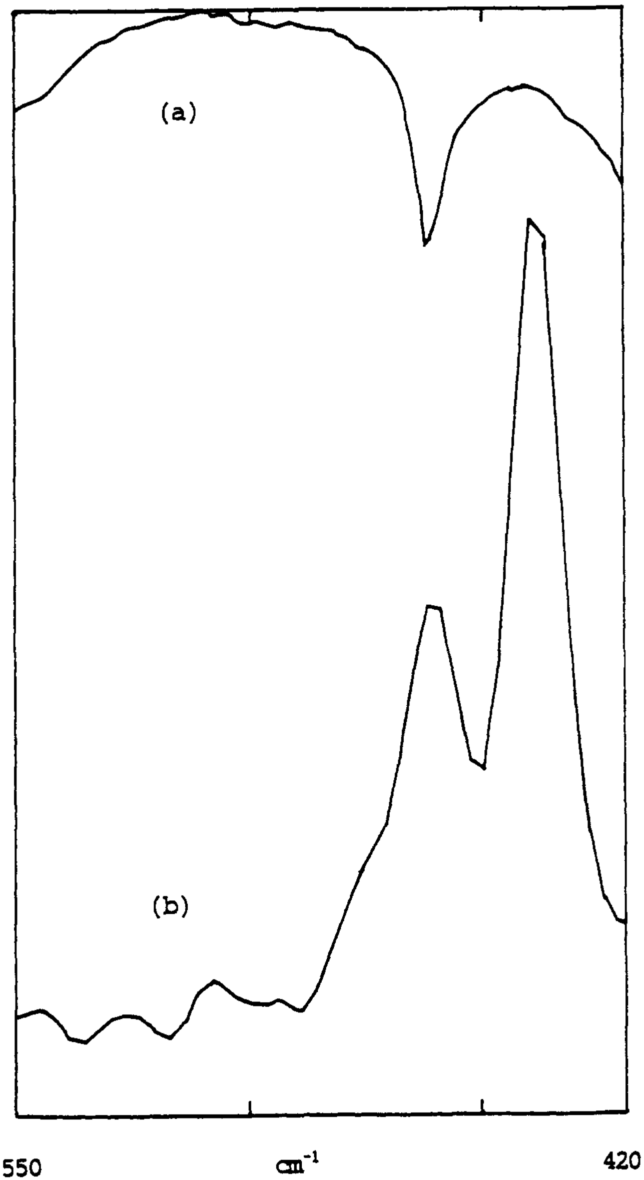

Figure 2. (a) FTIR and (b) FT Raman spectra of 1.

peak (seen in the UV spectrum of 2,2′-bipyridyl), which extends into the visible region and gives rise to the yellow color of the compound. Thus, if suitable volatile adducts of dimethylcadmium can be made, they may be more photosensitive than the pure alkyl and thus suited to photochemical MOVPE.

The ^{113}Cd, ^{13}C, and ^{1}H NMR spectra of 1 and dimethylcadmium (Table IV) were recorded in benzene-d_6. Comparison of the ^{1}H spectra of 1 and dimethylcadmium reveals that the methyl protons become deshielded (by ca. +0.09 ppm) on adduct formation, which is the reverse of the usual behavior.[15] In contrast the methyl resonance shift in the ^{13}C spectra is indicative of an increase in shielding (by −1.3 ppm) on adduct formation [$^{1}J(^{13}C–Cd)$ in free dimethylcadmium being 512.64 and 536.44 Hz for the two NMR-active Cd nuclides, namely ^{111}Cd and ^{113}Cd]. Finally, examination of the proton-decoupled ^{113}Cd spectrum of 1 and of dimethylcadmium shows that there is a shift upfield of 7.2 ppm on adduct formation. The proton coupled ^{113}Cd spectrum of 1 (Figure 3) has the expected septet structure [^{2}J(Cd–H) is 51.1 Hz in free dimethylcadmium, 52.0 Hz in 1]. However, there is line broadening as a result of further coupling to the protons of the bipyridyl rings. The ^{1}H and ^{13}C resonances of the 2,2′-bipyridyl moiety in 1 exhibit the expected differences from the spectra of the free ligand.

Table IV. ^{1}H, ^{13}C, and ^{113}Cd NMR Data[a,b] for Dimethylcadmium and (2,2′-Bipyridyl)dimethylcadmium(II)

dimethylcadmium	(2,2′-bipyridyl)-dimethylcadmium(II)	
	^{1}H	
−0.56 ppm (CH$_3$) [J(Cd–^{1}H)[c] = 50.00 Hz]	−0.45 ppm (CH$_3$) [J(^{113}Cd–^{1}H) = 48.11 Hz]	
	6.68 ppm (m)	ligand resonances
	7.16 ppm (t of d)	ligand resonances
	8.10 ppm (d of t)	ligand resonances
	8.42 ppm (d of q)	ligand resonances
	^{13}C	
−2.5 ppm [J(^{13}C–Cd)[d] = 512.6 and 536.4 Hz]	−3.8 ppm (CH$_3$)	
	149.2 ppm	ligand resonances
	136.6 ppm	ligand resonances
	123.7 ppm	ligand resonances
	121.1 ppm	ligand resonances
	^{113}Cd[a]	
545.0 ppm [J(^{113}Cd–^{1}H) = 51.1 Hz, ^{1}H coupling gives septet]	537.8 ppm [J(^{113}Cd–^{1}H) = 52.0 Hz, ^{1}H coupling gives septet]	

[a] ^{1}H and ^{13}C spectra referenced to (CH$_3$)$_4$Si. ^{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. [d] These couplings arise from the influence of the ^{113}Cd and ^{111}Cd nuclei.

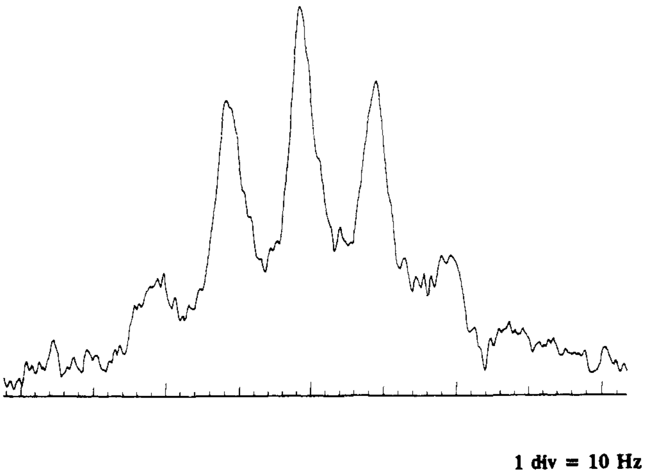

Figure 3. ^{113}Cd NMR spectrum of 1.

(c) Obtaining a Sample of Pure Dimethylcadmium from 1. In order to obtain a pure sample of dimethylcadmium from 1, the procedure outlined in the Experimental Section was followed. The purity of the dimethylcadmium obtained directly by heating 1 was assessed by studying infrared spectra of the vapor present over the liquid sample. We invariably found diethyl ether as an impurity. Pure dimethylcadmium was readily obtained by a three trap vacuum distillation using a dynamic system, as described in the Experimental Section.

Our results therefore show that great care is needed in obtaining pure samples of dimethylcadmium from 1 and that two stages are necessary. The use of two stages with 1 does however yield a pure sample of dimethylcadmium more rapidly and more easily than trap-to-trap distillation.[16]

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Conclusions

Our study has shown, contrary to previous reports, that dimethylcadmium does form a stable adduct with 2,2′-bipyridyl, 1, that exists in the solid and gas phases as well as in benzene and ethereal solutions. We find that full dissociation of the adduct in vacuo takes place only at ca. 70 °C and that this process is accompanied by some sublimation of the undissociated adduct. Consequently, care is needed to obtain pure dimethylcadmium by the thermal decomposition of 1. To overcome the problem, we are currently investigating the use of less volatile nitrogen-containing ligands.

The most noteworthy features of this structure are the large C–Cd–C angle of 148.4 (8)° and the angle of 79.0° between the C–Cd–C and N–Cd–C planes.

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Supplementary Material Available: Tables of bond distances and angles, thermal parameters, and H atom coordinates (3 pages); a listing of structure factors (8 pages). Ordering information is given on any current masthead page.

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