PREPARATION AND CHARACTERIZATION OF AMINE ADDUCTS OF ORGANOZINC AND CADMIUM COMPOUNDS. X-RAY CRYSTAL STRUCTURE OF DIETHYL(1,4-DIAZABICYCLO[2,2,2]OCTANE)ZINC(II)

Xiaoying Huang[1], Hongsui Sun*[2], Ximeng Wang[2], Yongi Jiang Liu[2],
Xiaozeng You[2] and Xiangzhen Sun[2]
[1] State Key Laboratory of Structure Chemistry, Fuzhou 350 002, China
[2] State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute,
Center for Advanced Studies in Science and Technology of Microstructures, Nanjing University,
Nanjing 210093, China

ABSTRACT:

The reaction of diethyl zinc (Et_2Zn) with 1,4-diazabicyclo[2,2,2]octane (dabco) and with acridine results in the formation of diethyl(1,4-diazabicyclo[2,2,2]octane)zinc(II) **1** and diethyl(bisacridine)zinc(II) **2** respectively. The reaction of dimethyl cadmium (Me_2Cd) with 5,6-benzoquinoline (BQ) gives dimethyl(bis-5,6-benzoquinoline)cadmium(II) **3**. Crystals of **1** are monoclinic, space group Pa with unit cell dimensions: $a=14.316(2)$, $b=7.871(2)$, $c=16.294(4)$Å, $\beta=91.21(2)°$ and $Z=2$. The structure was refined by a full-matrix least-squares procedure to final $R=0.049$ using 2192 reflections.

Keywords: Adduct, diethyl zinc, dimethyl cadmium, MOCVD precursors, X-ray crystal structure

INTRODUCTION:

The Metal-Organic Chemical Vapor Deposition (MOCVD) of III-V semiconductors from adducts of MR_3($M=Al$, Ga,In) with Lewis base has revealed some advantages over the trialkyl metal precursors [1]. Fire and toxicity hazards are less severe throughout the MOCVD process with these adducts than with the amine free organometals. The work about the synthesis and characterization of adduct precursors has been concentrated on Main Group elements, such as $[Al(CH_3)_3]_4$[N-tetramethylcyclam] [2], $[Al(CH_3)_3][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$ [3], $[In(CH_3)_3][L_N]$[4] (L_N=nitrogen containing Lewis base), $[Me_3M][L_P]$ [5] (L_P=phosphonium containing Lewis base), $[Me_3CCH_2)_3Ga\text{-}P(H)Ph_2]$, $[Me_3SiCH_2)_3Ga\text{-}P(H)Ph_2]$ [6], and $[Me_3Ga\text{-}L_N]$ [7]. Herein, we reported the synthesis and characterization of adducts of R_2M($R=Et$, $M=Zn$; $R=Me$, $M=Cd$) with Lewis base, together with the X-ray structure analysis of Et_2Zn-dabco **1**.

EXPERIMENTAL:

All reactions were performed by using Schlenk techniques under N_2 or in a Vacum Atmosphere HE-493 Dri-Train Drybox under N_2. Solvents were dried over Na benzophenone and distilled under N_2 prior to use. ^1H NMR spectra were obtained with a PMX-60 spectrometer in C_6D_6 using Me_4Si as internal reference. Mass spectra were obtained using ZAB-MS instrument. Microanalyses (C,H and N) were performed on a Cario-Erba 1106 carbon, hydrogen and nitrogen analyzer. Diethyl zinc and dimethyl cadmium were provided by the Special Gas Institute of Nanjing University. Dabco and acridine were purchased from commercial suppliers and used as received.

Synthesis of diethyl(1,4-diazabicyclo[2,2,2]octane)zinc(II) 1

A solution of dabco(11.2g, 0.1 mol) in 100 cm^3 E_2tO was added to a stirring solution of diethyl zinc(13.5cm^3, 0.1 mol) in 30 cm^3 Et_2O. A white precipitate was formed immediately. The reaction mixture was continuously stirred for 1 h at room temperature. The white precipitate was filtered off, washed with Et_2O and rescrystallized from hot benzene to give colorless needle crystals suitable for X-ray determination. Yield 90%. Anal.: Calcd. for $C_{10}H_{22}N_2Zn$: C, 50.95; H, 9.43; N, 11.89%. Found: C, 50.25; H, 8.81; N, 11.22%. NMR (^1H, C_6D_6, 25°C): δ, 0.55(q,4H,$2CH_2Zn$); 1.8(t,6H,$2CH_3$); 2.45(s,12H, $6CH_2N$)ppm. MS, m/z: 122(Et_2Zn), 112(dabco), 64(Zn), 58(Et), 56[$N(CH_2)_3$], 42[$(CH_2)_3$].

Synthesis of diethyl(bisacridine)zinc(II) 2

To a stirring solution of diethyl zinc(1.5cm^3, 14.3 mmol) in 15 cm^3 Et_2O was added a solution of acridine(2.5, 14 mmol) in 60 cm^3 Et_2O. Orange red solution was obtained and stirred for 2 h. Solvent was removed in vacuo and the deep orange microcrystals were dissolved in Et$_2$O. After cooling to -40°C for 4 h, dark red crystals were obtained. Yield 65%. Anal.: Calcd. for $C_{30}H_{28}N_2Zn$: C, 74.8; H, 5.8; N, 5.8%. Found: C, 73.5; H, 5.1; N, 5.3%. NMR(^{1}H,C$_6$D$_6$,25°C): δ, 0.92(m,CH$_2$Zn); 2.9(t,CH$_3$; 6.7-7.0, 7.2-7.6, 8.4(m,acridine ring)ppm. MS, m/z: 272(M-Et), 179(acridine), 122(Et$_2$Zn), 93(ZnEt), 64(Zn).

Synthesis of dimethyl(bis-5,6-benzoquinoline)cadimium(II) 3

To a stirring solution of 5,6-benzoquinoline(2g, 11.2 mmol) in 60 cm^3 Et$_2$O was added dimethyl cadmium(0.96cm^3, 13.4 mmol). The reaction mixture was continuously stirred for 2 h. Solvent was removed and the resulting white solid was recrystallized from cyclohexane to give **3** as white needle crystals. Yield 80%. Anal.: Calcd. for $C_{28}H_{24}N_2Cd$: C, 67.2; H, 4.8; N, 5.6%. Found: C, 67.5; H, 4.7; N,5.2%. NMR (^{1}H, C$_6$D$_6$, 25°C): δ 0.4(s,CH$_3$), 7.0-7.7,8.3-8.4,9.0(m,BQ ring)ppm. MS,m/z:179(BQ),144(CdMe$_2$), 129(CdMe).

Determination of crystal structure of Et$_2$Zn-dabco 1

An air and moisture sensitive crystal of dimensions 0.6 X 0.3 X 0.3 mm, which was sealed in a glass capillary, was mounted on an Enraf-Nonius CAD4 diffractometer [8] (using MoKα radiation, λ=0.71069Å.) Accurate cell dimensions and space group data were obtained from 25 strong reflections in the $27.94° < 2\theta < 29.84°$ shell. The ω-2θ scan technique was employed to measure the intensities of 4036 reflections such that θ_{max} was 26°.

The structure was solved by direct methods (MITHRIL) [9] and refined by the full-matrix least-squares method. Atomic scattering factors and anomalous dispersion terms were taken from Ref. 10. All calculations were carried out on a Micro VAX 3100 computer using the TEXSAN program [11]. The parameters used in data collection and processing as well as the final discrepancy factors at the conclusion of the refinement are given in Table 1.

Table 1 Crystal data and refinment details for 1

Formular	$C_{30}H_{66}N_6Zn_3$
Formular weight	707.03
Crystal systerm	monoclinic
Space group	Pa(7#)
Cell constants	a=14.316(2)Å
	b=7.871(2)Å
	c=16.294(4)Å
	β=91.21(2)°
	V=1835.6(8)Å^3
Z	2
D_{calc}	1.28g/cm^3
F(000)	756
μ(Mo-Kα)	20.19cm^{-1}
$2\theta_{max}$	51.9°
Range of h,k,l	h=0-17; k=0-9; l=-20-20
No. of reflections measured	4036
No. of indipendent reflections	3899
No. of observed reflections	2192
No. of reflections used in refinement	2192
No. of parameters refined	350
Weighting scheme	$w=1/\sigma^2(F)$
R	0.049
R_w	0.054
$\Delta\rho_{max}$	0.32e/Å^3
$\Delta\rho_{max}$	-0.35e/Å^3

RESULTS AND DISCUSSION

R_2M($R=Et$, $M=Zn$; $R=Me$, $M=Cd$) react with the Lewis bases e.g. 1,4-diazabicyclo [2,2,2]octane, acridine and 5,6-benzoqunoline to give the Lewis acid-base adducts **1-3**(Scheme 1):

$$R_2M \ + \ nL \qquad\qquad R_2M\text{-}L_n$$

1	R=Et,	M=Zn,	L=dabco	n=1
2	R=Et,	M=Zn,	L=acridine	n=2
3	R=Me,	M=Cd,	L=BQ	n=2

Scheme 1

The adducts, especially **1** and **2**, are very much sensitive towards air and moisture, though they are not flammble. So the satisfactory C, H, N measurement are difficult to obtain.

Table 2 Selected position parameters and their estimaed standard deviations

atom	X	Y	Z	B(eq)
Zn(1)	0.8870	-0.1414(1)	0.6643	4.12(5)
Zn(2)	0.7144(3)	0.3445(3)	0.3197(3)	4.7(2)
Zn(3)	1.0605(3)	0.3470(3)	0.0074(3)	4.0(1)
N(1)	0.931(1)	0.039(2)	0.764(1)	4.3(8)
N(2)	0.990(1)	0.202(2)	0.895(1)	3.2(8)
N(3)	0.845(1)	0.043(2)	0.558(1)	3.6(8)
N(4)	0.792(1)	0.201(3)	0.426(1)	4(1)
N(5)	0.824(1)	0.336(2)	0.221(1)	4.4(9)
N(6)	0.942(1)	0.333(2)	0.102(1)	3.9(8)
C(1)	1.017(2)	0.120(3)	0.752(1)	8(2)
C(2)	1.045(2)	0.219(4)	0.827(2)	8(1)
C(3)	0.944(2)	-0.071(3)	0.842(1)	4(1)
C(4)	0.983(2)	0.016(3)	0.911(1)	6(1)
C(5)	0.863(2)	0.157(3)	0.793(2)	6(1)
C(6)	0.909(2)	0.258(4)	0.865(2)	10(2)
C(7)	0.753(1)	0.130(3)	0.570(1)	5(1)
C(8)	0.721(2)	0.224(4)	0.493(1)	7(1)
C(9)	0.912(2)	0.181(4)	0.539(2)	7(1)
C(10)	0.888(2)	0.263(3)	0.454(1)	6(1)
C(11)	0.829(2)	-0.073(3)	0.498(2)	7(1)
C(12)	0.802(2)	0.021(3)	0.409(1)	8(1)
C(13)	0.859(3)	0.178(4)	0.208(2)	9(2)
C(14)	0.928(3)	0.155(3)	0.137(2)	6(1)
C(15)	0.909(2)	0.401(4)	0.254(1)	9(1)
C(16)	0.984(2)	0.416(4)	0.178(1)	9(2)
C(17)	0.793(2)	0.419(5)	0.153(2)	10(2)
C(18)	0.855(2)	0.433(4)	0.089(1)	8(1)
C(19)	1.004(2)	-0.236(4)	0.629(2)	8(2)
C(20)	1.042(2)	-0.395(3)	0.656(2)	16(2)
C(21)	0.765(1)	-0.237(3)	0.702(1)	5(1)
C(22)	0.776(1)	-0.403(2)	0.737(1)	7(1)
C(23)	0.716(2)	0.575(3)	0. 354(2)	5(1)
C(2$)	0.631(2)	0.630(2)	0.405(1)	6(1)
C(25)	0.621(2)	0.173(3)	0.2 81(2)	6(1)
C(26)	0.538(2)	0.174(3)	0.328(2)	7(1)
C(27)	1.156(2)	0.186(3)	0.053(1)	6(1)

Table 3 Selected bond angles of 1

atom	atom	distance(Å)	atom	atom	atom	angle(°)
Zn(1)	C(19)	1.93(3)	C(19)	Zn(1)	C(21)	135.3(5)
Zn(1)	C(21)	2.02(2)	C(19)	Zn(1)	N(1)	103(1)
Zn(1)	N(1)	2.24(2)	C(19)	Zn(1)	N(3)	104(1)
Zn(1)	N(3)	2.33(1)	C(21)	Zn(1)	N(1)	104.2(8)
Zn(2)	C(23)	1.90(2)	C(21)	Zn(1)	N(3)	104.4(9)
Zn(2)	C(25)	2.00(2)	N(1)	Zn(1)	N(3)	102.2(3)
Zn(2)	N(5)	2.27(2)	C(1)	N(1)	C(5)	111(2)
Zn(2)	N(4)	2.33(2)	C(1)	N(1)	C(3)	107(2)
Zn(3)	C(27)	2.00(3)	C(1)	N(1)	Zn(1)	114(1)
Zn(3)	C(29)	2.10(2)	C(5)	N(1)	C(3)	100(2)
Zn(3)	N(6)	2.32(2)	C(5)	N(1)	Zn(1)	118(1)
Zn(3)	N(2)*	2.37(2)	C(3)	N(1)	Zn(1)	106(1)
N(1)	C(1)	1.41(3)				
N(1)	C(5)	1.43(3)				
N(1)	C(3)	1.55(3)				
C(1)	C(2)	1.50(3)				
C(3)	C(4)	1.42(3)				
C(5)	C(6)	1.56(4)				

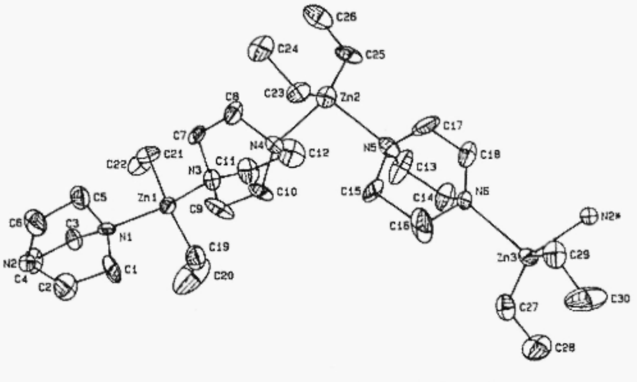

Figure 1 Molecular structure of 1 showing 30% probability displancement ellipsoids

The results of the X-ray work are summarized in Tables 2 and 3. As shown in Figure 1, the metal atom of diethyl(1,4-diazabicyclo[2,2,2]octane) zinc(II) is four coordinated and exhibits a distorted tetrahedral geometry with C-Zn-C angles are larger(135-138°) than N-Zn-C(102-104°). The 1:1 adduct of 1 forms molecular chains in the cell like Me_3In-dabco [12] and Me_2Cd-dabco [13]. This is due to the fact that Zn, Cd, In atmos are large enough to accommodate two coordinated nitrogen atoms. The In-N and Zn-C bond lengths are in the range of 2.24-2.37Å and 1.90-2.10Å respectively. The zinc and nitrogen atoms in the chain are nearly co-planer[Zn(1), Zn(2), Zn(3), N(3), N(4), N(5), (6)].

Acridine and 5,6-benzoquinoline, as monodentate Lewis bases, form 2:1 adducts with Et_2Zn and Me_2Cd respectively.

^1H NMR spectra of compounds 1-3 are listed in experimental section. It is noteworthy that the chemical shift of CH_3

and CH_2 in $(CH_3CH_2)_2Zn$ have significant shift in compounds **1** and **2**. The $CH_3(\delta,0.92ppm)$ and $CH_2(\delta,2.9ppm)$ proton signals in compound **2** are shifted downfield compared with $CH_3(\delta,0.55ppm)$ and $CH_2(\delta,1.8ppm)$ in compound **1** , this is due to the delocalization of electron density from the metal to the BQ rings in compound **2**. P.T.Narasimhan and cowers[14] gave a ditail dissussion on ^1H NMR of ethyl compounds. Comparing with their observation, the relative chemical shifts between methyl and methylene groups in compounds **1** and **2** are biger. Because both in compound **1** and **2**, nitrogen coordinated to the zinc would increase the electron density on the metal and methylene groups, hence the δCH_2 would shift to upfield.

Mass spectra of compounds **1** and **2** showed the Et_2Zn and dabco, acridine fragments respectively. Me_2Cd and BQ fragments were found in compound **3**. All compounds did not showed the parent molecular ion $[M]^+$.

ACKNOWLEDGEMENTS:

This work was supported by the National Nature Science Foundation, and a grant for the Key Research Project from the State Science and Technology Commission , and Post-doctoral Foundation of China.

REFERENCE:

1. Moss R.H., *J.Cryst.Growth.*,1984, **68**,78-87.
2. Robinson G.H., Zhang H. and Atwood J.L., *J.Organomet.Chem.*,1987, **331**, 153-160.
3. Robinson G.H., Lee B., Pennington W.T. and Sangokoya S.A., *J.Am.Chem.Soc.*, 1988, **110**, 6260-6261.
4. Foster D.F., Rushworth S.A., Cole-Hamiton D.J., Cafferty R., Harrison J., and Parkes P., *J.Chem.Soc.Dalton Trans.*,1988, 7-11.
5. Bradley D.C., Chudzynska H., Faktor M.M., Frigo D.M., Hursthouse M.B., Hussain B. and Smith L.M., *Polyhedron*, 1988, **7**,1289-1298.
6. Banks M.A., Beachley,Jr.O.T. and Maloney J.D., *Polyhedron*,1990, **9**, 335-342.
7. Bradley D.C., Dawes H.M., Hursthouse M.B., Smith L.M. and Thornton-pett M., *Polyhedron*, 1990, **9**, 343-351.
8. Enraf-Nonius, *CAD4 Operation Manual*, Version 5.0,(1989). Delft Instruments X-ray Diffraction PO BOX 811, 2600 AV Delft, The Netherland.
9. Gilmore G.J., *MITHRIL*, (1983). A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data. University of Glasgow, Scotland.
10. Ibers J.A. and Hamilton W.C.(Eds), *International Tables for X-ray Crystallography*, Vol. IV, Kynoch press, Birmingham,(1974).
11. Molecular Structure Corporation, *TEXAN, TEXRAY Structure Analysis Package*, Revised(1987), MSC, 3200A Research Forest Drive, The Woodlands,TX77381,USA.
12. Bradley D.C., Dawes H.M., Frigo D.M., Hursthouse M.B. and Hussain B., *J.Organomet.Chem.*, 1987, **325**,55-67..
13. Wang X., Sun H., Sun X., You X. and Huang X., *Acta Cryst.*, 1995,**C51**,1754-1756.
14. Narasimhan P.T. and Roger M.T., *J. Am Chem Soc.*,1960, **82**, 5983-5986.

Received: November 15, 1995 - Accepted: December 18, 1995 - Accepted in revised camera-ready format: January 15, 1996