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Dimethylzinc adducts with macrocyclic amines

Kathleen M. Coward,[a] Anthony C. Jones,*[a] Alexander Steiner,[a] Jamie F. Bickley,[a] Lesley M. Smith[b] and Martyn E. Pemble[c]

[a] *Department of Chemistry, University of Liverpool, Liverpool, UK L69 7ZD*
[b] *Epichem Limited, Power Road, Bromborough, Wirral, UK CH62 3QF*
[c] *Department of Chemistry, University of Salford, Salford, UK M5 4WT*

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The structures of dimethylzinc adducts with the macrocyclic amines 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, **1**, and 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane, **2**, have been determined by X-ray diffraction analysis. The adducts each contain two dimethylzinc moieties. In **1** the dimethylzinc moiety forms a six-membered chelate ring with adjacent nitrogen atoms, in preference to the more sterically strained 5-membered ring. In **2** dimethylzinc exists in a 5-membered chelate ring configuration. Compounds **1** and **2** can be used as intermediate adducts in the adduct purification of dimethylzinc for use in the MOCVD of II–VI and III–V materials.

Introduction

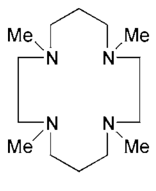
Tertiary amine adducts of Group 12 alkyls have been known for many years,[1–3] but relatively little structural information exists for these compounds. Recently there has been revived interest in adducts of dimethylzinc (Me_2Zn) and diethylzinc (Et_2Zn) as they are useful both as precursors in metalorganic chemical vapour deposition (MOCVD)[4–7] and in the purification of metal alkyls for subsequent use in MOCVD.[8,9]

For instance, $ZnMe_2(NEt_3)$ has been used as a precursor for the MOCVD of ZnSe and ZnS[4,6] and as a p-type dopant source for III–V materials such as GaAs, AlGaAs.[5,7] Less volatile adducts such as $[ZnR_2\{(C_5H_4N)(CH_2)_3(C_5H_4N)\}]_n$ have been used for the purification of Me_2Zn and Et_2Zn[8,9] in which electronic grade alkyls are produced by the mild thermal dissociation of the adduct.

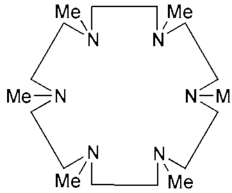
A particular advantage in using tertiary amines for the adduct purification of R_2Zn compounds is that alkyl iodides MeI and EtI (common contaminants in Grignard-based synthesis reactions) are chemically removed by precipitation of the involatile $R_4N^+I^-$ salt.[6] This has important implications for precursors used in II–VI epitaxy as alkyl halides are highly efficient n-type dopants.[6] Furthermore, tetrameric alkoxyzinc species $[ZnMe(OMe)]_4$, which can contribute to reduced luminescence efficiency Zn-doped AlGaAs and AlGaInAs,[10] are unlikely to complex with the tertiary amine, and can thus be removed by recrystallisation of the $R_2Zn(L)$ adduct.

The amine ligand used in adduct purification must form a relatively weak donor–acceptor bond with the metal alkyl, allowing adduct dissociation at relatively low temperature (<150 °C) and must be significantly less volatile than the liberated alkyl to allow easy separation. There are relatively few nitrogen donors which fulfil these criteria, for example Me_2Zn cannot be recovered from the complexes $ZnMe_2[Me_2N(CH_2)_2NMe_2]$,[11] $ZnMe_2[(CH_2NMe)_3]_2$[12] and the Me_2Zn adduct of (−)sparteine.[13] However, quantitative yields of Me_2Zn and Et_2Zn have been obtained by thermal dissociation of their adducts with the high molecular weight amine 1,3-bis(4-pyridyl)propane $(C_5H_4N(CH_2)_2C_5H_4N)$[9] and this has led us to explore the use of other high molecular weight amines.

We have recently shown[14] that the macrocyclic amines 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (abbrev. N_4-aza crown) and 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane (abbrev. N_6-aza crown) form reversible adducts with triethylgallium and triisopropylgallium. In this paper we report the synthesis and full structural characterisation of the analogous dimethylzinc adducts, $(Me_2Zn)_2[N_4\text{-aza crown}]$ and $(Me_2Zn)_2[N_6\text{-aza crown}]$, and a comparison is made with the structure and properties of other Me_2Zn–tertiary amine adducts. Although the adducts $(Me_3Al)_4[N_4\text{-aza crown}]$,[15] $(Me_3Ga)_4[N_4\text{-aza crown}]$,[16] $(R_3Ga)_4[N_4\text{-aza crown}]$[14] and $(R_3Ga)_6[N_6\text{-aza crown}]$[14] are known, the complexes described herein are the first reported Group II alkyl adducts with macrocyclic amines.



N_4–aza crown



N_6–aza crown

Experimental

General techniques

Me_2Zn was a gift from Epichem Limited. The nitrogen donor ligands 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (N_4-aza crown) and 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane [N_6-aza crown] were purchased from Aldrich Chemical Co. and dried by storage over molecular sieves prior to use.

^1H NMR spectra were obtained using a Bruker 300 NMR spectrometer and infrared spectroscopy was carried out on a Perkin-Elmer 1000 infrared Fourier Transform spectrometer using a Nujol mull pressed between NaCl plates.

Elemental microanalyses were carried out by the Chemistry Department service at Liverpool University and fast atom bombardment (FAB) mass spectroscopy was performed on a DEC Vax 4000.60 using 3-nitrobenzyl alcohol as matrix.

Synthesis of Me_2Zn adducts with macrocyclic amines

The synthesis method used for compounds **1** and **2** involved the addition of Me_2Zn (1 mol equivalent) to a stirred suspension of the macrocyclic amine in toluene, N_4-aza crown (0.50 mol

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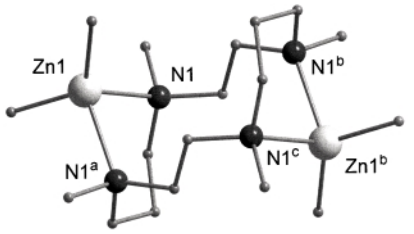

Fig. 1 Crystal structure of $(Me_2Zn)_2[N_4$-aza crown] **1**.

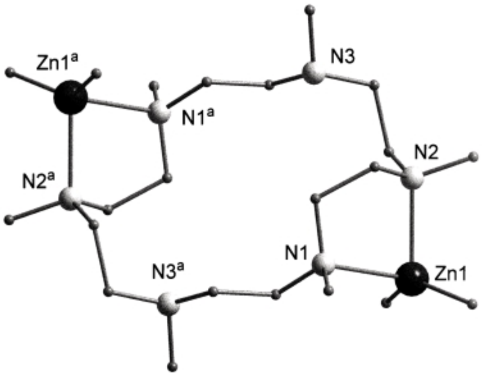

Fig. 2 Crystal structure of $(Me_2Zn)_2[N_6$-aza crown] **2**.

equivalent) or N_6-aza crown (0.50 mol equivalent). Removal of the toluene *in vacuo* gave the adducts **1**, **2** as crystalline solids. They were characterised by ^1H NMR spectroscopy, elemental microanalysis and infrared (IR) spectroscopy. Slow recrystallisation from toluene produced crystals of suitable quality for X-ray diffraction studies.

$(Me_2Zn)_2[N_4$-aza crown] 1. Colourless crystalline solid. mp 123–125 °C. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 0.0 [s, 12 H, $ZnCH_3$], 1.2 [m, 4 H, $CH_2CH_2CH_2$], 1.84 [s, 12 H, NCH_3] and 2.10–2.20 [bs, 16 H, $NCH_2CH_2CH_2N$, NCH_2CH_2N]. Found: C, 47.83; H, 9.60; N, 12.24%. Calc. for $C_{18}H_{44}N_4Zn_2$: C, 48.32; H, 9.93; N, 12.53%. IR (Nujol)/cm^{-1}: 2079w, 1669m, 1603m, 1356m, 1302m, 1265m, 1215w, 1171m, 1044s, 1002s, 967s, 927m, 804s, 728s and 654s. FAB MS (*m/z*): 335.2, $[MeZn(N_4$-aza crown)]$^+$; 320.2, $[Zn(N_4$-aza crown)]$^+$; and 257.2, $[N_4$-aza crown]H$^+$.

$(Me_2Zn)_2[N_6$-aza crown] 2. Colourless crystalline solid. Mp 157–158 °C. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 0.0 [s, 12 H, $ZnCH_3$], 2.4 [s, 18 H, NCH_3] and 2.90 [bs, 24 H, NCH_2CH_2N]. Found: C, 49.41; H, 10.11; N, 15.49%. Calc. for $C_{22}H_{54}N_6Zn_2$: C, 49.52; H, 10.22; N, 15.75%. IR (Nujol)/cm^{-1}: 2248w, 1676w, 1603w, 1352m, 1315m, 1296m, 1272s, 1232w, 1168w, 1130s, 1115m, 1096s, 1068m, 1029s, 983w, 946s, 925s, 825m, 769s, 745s, 656s and 618s. FAB MS (*m/z*): 436.2, $[Me_2Zn(N_6$-aza crown)]$^+$; 421.2, $[MeZn(N_6$-aza crown)]$^+$; 407.2, $[Zn(N_6$-aza crown)]$^+$; and 341.2, $[N_6$-aza crown]$^+$.

Single crystal X-ray diffraction

Single crystals of $(Me_2Zn)_2[N_4$-aza crown] **1** and $(Me_2Zn)_2[N_6$-aza crown] **2** suitable for X-ray diffraction were obtained by the slow recrystallisation of each adduct from toluene. Crystallographic data were recorded on a Stoe-IPDS dffractometer using graphite monochromated Mo-Kα-radiation (wavelength = 0.71073 Å), $T = 200$ K. Structures were solved by Direct Methods and refined by full-matrix least squares against F^2 using all data.[17] Crystal and data collection parameters are given in Table 1.

CCDC reference number 186/2128.

See http://www.rsc.org/suppdata/dt/b0/b006253g/ for crystallographic files in .cif format.

Table 1 Crystal and data collection parameters for $(Me_2Zn)_2[N_4$-aza crown] **1** and $(Me_2Zn)_2[N_6$-aza crown] **2**

	1	**2**
Empirical formula	$C_{18}H_{44}N_4Zn_2$	$C_{22}H_{54}N_6Zn_2$
Formula weight	447.40	533.56
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_1/n$	*Pnnm*
a/Å	10.519(3)	12.500(2)
b/Å	11.153(3)	8.1763(8)
c/Å	9.575(5)	14.442(2)
β/°	90.000	109.052(18)
V/Å^3	1123.2	1395.2(3)
Z	2	2
Reflections collected	2862	8557
Reflections unique (R_{int})	813 (0.0377)	2171 (0.0471)
$R1$ [$I > 2\sigma(I)$]	0.0312	0.0318
$wR2$ (all data)	0.0764	0.0803

Table 2 Selected bond distances (Å) and angles (°) for $(Me_2Zn)_2[N_4$-aza crown] **1** and $(Me_2Zn)_2[N_6$-aza crown] **2**

$(Me_2Zn)_2[N_4$-aza crown]			
C(1)–Zn(1)	2.012(5)	C(3)–N(1)	1.477(5)
C(2)–Zn(1)	2.032(6)	C(4)–N(1)	1.485(5)
N(1)–Zn(1)	2.282(3)	C(5)–N(1)	1.486(5)
C(1)–Zn(1)–C(2)	125.5(2)	C(2)–Zn(1)–N(1)	103.07(14)
C(1)–Zn(1)–N(1)	115.36(13)	N(1)–Zn(1)–N(2)	87.19(1)
$(Me_2Zn)_2[N_6$-aza crown]			
C(1)–Zn(1)	2.000(3)	C(7)–N(2)	1.474(3)
C(2)–Zn(1)	2.000(3)	C(8)–N(2)	1.473(3)
C(4)–N(1)	1.482(3)	C(9)–N(2)	1.480(3)
C(5)–N(1)	1.472(4)	C(10)–N(3)	1.470(3)
C(6)–N(1)	1.480(3)	C(11)–N(3)	1.469(3)
N(1)–Zn(1)	2.331(2)	N(2)–Zn(1)	2.257(2)
C(2)–Zn(1)–C(1)	138.10(13)	C(2)–Zn(1)–N(1)	106.51(11)
C(2)–Zn(1)–N(2)	103.79(10)	C(1)–Zn(1)–N(1)	104.49(11)
C(1)–Zn(1)–N(2)	108.64(11)	N(2)–Zn(1)–N(1)	80.35(7)

Results and discussion

The structures of compounds **1** and **2** as determined by X-ray crystallography are shown in Figs. 1 and 2, and important bond lengths and angles are summarised in Table 2. The structures consist of molecular units with distorted tetrahedral coordination at zinc. In **1** the Me_2Zn forms two six-membered chelate rings with adjacent nitrogen donor sites, similar to the configuration of Me_2Zn in the Me_2Zn–(−)sparteine complex.[13] In **1** the six-membered configuration around Me_2Zn is clearly favoured over the more sterically strained five membered configuration. In **2** the Me_2Zn forms two five-membered [N–Zn–N] chelate rings, similar to the configuration of Me_2Zn in the $ZnMe_2[Me_2N(CH_2)_2NMe_2]$ adduct.[11] Whilst the N_4-aza crown adduct has a predictable Me_2Zn : ligand stoichiometry of 2 : 1, steric constraints in the N_6-aza crown adduct limit the stoichiometry to 2 : 1.

The C–Zn–C bond angles in adducts **1** and **2** of 125 and 138°, respectively, are larger than expected for an angle at a tetrahedral centre (109°), while the N–Zn–N angles (87.19(1), 80.35(7)°) are smaller. However, the C–Zn–N angles (103.07(14), 104.49(11)°) are close to the ideal tetrahedral angle, and similar distorted tetrahedral geometries around Zn have previously been reported for the adducts $ZnMe_2$-$[Me_2N(CH_2)_2NMe_2]$,[11] Me_2Zn(−)-sparteine[13] and $[ZnMe_2\{(C_5H_4N)(CH_2)_3(C_5H_4N)\}]$.[9] The distorted tetrahedral configuration commonly observed[9,11,13] in Me_2Zn amine adducts has been attributed to electronic rather than crystal packing effects.[9] Generally, the C–Zn–C angle in zinc alkyl amine

Table 3 Selected bond lengths and angles for some structurally characterised zinc alkyl amine adducts

	Bond lengths/Å		Bond angles/°		
Compound	Zn–C	Zn–N	C–Zn–C	N–Zn–N	Ref.
$(Me_2Zn)_2[N_4$-aza crown]	2.012(5)	2.282(3)	125.5(2)	87.18	This work
$(Me_2Zn)_2[N_6$-aza crown]	2.000(3)	2.331(2)	138.10(13)	80.35(7)	This work
$ZnMe_2[(C_5H_4N)CH_2CH_2CH_2(C_5H_4N)]$	2.000(5)[a]	2.241(3)	145.5(2)	98.4(1)	9
$ZnMe_2[(CH_2NMe)_3]_2$	1.987(6)[a]	2.410(4)	145.1(2)	100.3(2)	20, 21
$ZnMe_2[(Me_2N(CH_2)_2NMe_2]$	1.982(4)[a]	2.269(8)[a]	135.8(3)	79.8(3)	11
$Me_2Zn(-)$–sparteine	2.012(8)[a]	2.239(6)[a]	128.2(4)	80.4(2)	13
$ZnMe_2(^tBu$-DAB)	2.003(2)[a]	2.216(7)[a]	137.3(3)	75.0(2)	22

[a] Average value.

adducts is much larger than 109°, lying in the range 125.5(2)–145.5(2)°, and this is thought to arise because the Zn atom uses only the s and p_z orbitals in forming the Zn–C bonds, whilst the p_x and p_y orbitals act as the acceptor orbitals for binding the nitrogen donor molecules.[9,18]

The Zn–C bond lengths in adducts **1** (2.012(5), 2.032(6) Å) and **2** (2.000(3) Å) are longer than those in base-free Me_2Zn (1.930 Å), shown by electron diffraction to be a linear molecule.[19] Similar Zn–C bond lengths (2.012(8) Å) have been reported in the $Me_2Zn(-)$–sparteine[13] and $[ZnMe_2\{(C_5H_4N)(CH_2)_3(C_5H_4N)\}]$,[9] adducts although the Zn–C bond lengths in $ZnMe_2[Me_2N(CH_2)_2NMe_2]$ are shorter at 1.974(9) and 1.989(9) Å.

The Zn–N bond distances in adducts **1** and **2** are unexceptional and fall within the range of 2.078(7) and 2.410(4) Å reported for other Me_2Zn–tertiary amine adducts (see Table 3) and the N–Zn–N bite angle is also comparable.

The compounds **1** and **2** were both shown to liberate base-free Me_2Zn (confirmed by ^1H NMR spectroscopy) when heated at 90–120 °C *in vacuo*, indicating that **1** and **2** are suitable for the adduct purification of Me_2Zn. It is interesting that heating the $Me_2Zn(-)$–sparteine adduct failed to liberate Me_2Zn.[13] This is somewhat surprising, as this complex has a similar distorted tetrahedral configuration and closely comparable Zn–N bond distances to those of **1** and **2** (see Table 3), and may indicate that the presence of a methyl group on the donor nitrogen atoms in **1** and **2** facilitates thermal dissociation of the adducts.

Conclusion

Me_2Zn forms adducts with macrocyclic amines of the type $(Me_2Zn)_2[N_4$-aza crown] and $(Me_2Zn)_2[N_6$-aza crown]. These adducts thermally dissociate at relatively low temperatures (120 °C or less), making them suitable for the adduct purification of Me_2Zn for use in the MOCVD of II–VI and III–V materials.

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