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Structural studies of some Group 12 metal alkyl adducts: the X-ray crystal structures of $Me_2Zn[Me_2N(CH_2)_2NMe_2]$, $Me_2Cd[Me_2N(CH_2)_2NMe_2]$, $(Me_3CCH_2)_2Zn[Me_2N(CH_2)_2NMe_2]$ and $(Me_3CCH_2)_2Cd[Me_2N(CH_2)_2NMe_2]$

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Abstract

The X-ray crystal structures of a series of group 12 metal alkyl adducts $Me_2M[Me_2N(CH_2)_2NMe_2]$ {M = Zn (**1**), Cd (**2**)} and $(Me_3CCH_2)_2M[Me_2N(CH_2)_2NMe_2]$ {M = Zn (**3**), Cd (**4**)} have been determined. Each adduct exists as a mononuclear, molecular unit with pseudo-tetrahedral coordination at the metal centre. Compound **1** crystallizes in space group $P2_1/a$, $a = 13.868(3)$, $b = 11.616(2)$ and $c = 7.588(2)$ Å, $\beta = 94.83(2)°$, compound **2** in space group *Cmca*, $a = 11.196(2)$, $b = 12.179(2)$ and $c = 17.969(3)$ Å. Compounds **3** and **4** are isostructural in space group $C2/c$ with the following unit cell dimensions for Zn {Cd}: $a = 17.167(5)$ {17.604(5)}, $b = 9.369(3)$ {9.484(3)}, and $c = 12.916(3)$ {12.758(3)} Å, $\beta = 107.83(2)$ {106.07(2)}°. Compound **1** and the parent alkyl of **4** have been used successfully in the growth of thin films by metalloorganic chemical vapour deposition, **1** as a dopant in the growth of p-type GaAs, and $[Me_3CCH_2]_2Cd$ as a Group 12 source in the growth of CdS.

1. Introduction

A number of Group 12 metal alkyl adducts with nitrogenous bases were reported nearly 30 years ago in a series of papers by Thiele [1–5]. The compounds prepared included adducts with both monodentate (*e.g.* triethylamine, pyridine) and bidentate ligands (*e.g.* 2,2-bipyridyl, 1,10-phenanthroline). The adducts with monodentate ligands were low-boiling liquids and both the 1:1 or 2:1 stoichiometries were investigated. Cryoscopic molecular weight measurements indicated that, in non-polar solvents such as benzene, extensive dissociation occurred for the 2:1 species and that these liquids are best viewed as equilibrium mixtures of the 1:1 adduct, the free amine and the 2:1 species. The liquids of 2:1 stoichiometry showed a marked tendency toward disproportionation on repeated vacuum distillation and eventually approached a stable 1:1 stoichiometry. Adducts with bidentate ligands were volatile solids, those with aromatic heterocyclic ligands forming brightly colored complexes due to metal-to-ligand charge-transfer transitions; the electronic spectra of such compounds have been investigated [6]. The M–N bond strength increases with the size of the alkyl group, the bigger alkyl groups providing more electron density, reducing the Lewis acidity of the metal but increasing back donation to the ligand. Due to the weak (b-type "soft") acceptor properties of cadmium, the adducts of its alkyls were more susceptible to dissociation than those of zinc [7].

Although such adducts have been known for many years, there is virtually no structural information. We have recently reported the first crystal structure of a simple adduct of dimethylzinc [8] (a bis complex with 1,3,5-trimethylhexahydro-1,3,5-triazine) and Pajerski *et al.* [9] have studied a rotoxane complex, Et_2Zn(18-

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crown-6), in which the linear C–Zn–C unit is maintained once the alkyl is threaded through the macrocycle. A number of studies of chelating ligands, $Zn[(CH_2)_3X]_2$ (where X = NMe_2 [10], OMe [11], SMe [10] and PPh_2 [12]) have been reported, Such work has involved characterization by electron and/or X-ray diffraction. In a formal sense, these compounds have similar first coordination spheres as the adducts studied in the present work, *i.e.* E_2ZnC_2.

There are no structures of adducts of simple cadmium alkyls or chelates of the kind described above. The X-ray crystal structures of a highly hindered functionalized alkyl, $M\{NC_5H_4C(SiMe_3)_2\}_2$ (M = Zn, Cd), have been reported by Henderson *et al.* [13]; the pyridyl function coordinates to the metal providing coordinative saturation (Cd–C 2.27 and Cd–N 2.49 Å). Other examples of crystallographically characterized organometallic cadmium species include: the adduct of the sterically hindered alkyl $(Me_3SiCH_2)_2Cd$ with 2,2′bipyridyl [14] (Cd–C 2.14 Å (av)), a trimeric phosphido complex of cadmium [15] (Cd–C 2.13–2.18 Å) and $(Me_2NCH_2C_6H_4)_2Cd$, the only characterized cadmium aryl [16] (Cd–C 2.154 Å).

A renewed interest in the chemistry of such metal alkyls can be traced to the use, by Manasevit, of trimethylgallium in conjunction with arsine to grow high quality epitaxial layers of GaAs by metallo-organic chemical vapour deposition (MOCVD) or metallo-organic vapour phase epitaxy (MOVPE) [17]. This technique was subsequently applied to the growth of II–VI materials using similar precursors; in recent years, there have been significant increases in the quality of the layers grown [18–20]. These improvements can be attributed to several factors, including improved reactor design, purer group 16 sources and the use of group 12 adducts [21–25].

Adduct precursors have several advantages including:

(1) better control of the vapour pressure; many alkyls are really too volatile for effective use (*e.g.* dimethylzinc, 124 Torr at 0°C [26]).

(2) purification of metal alkyl precursors. The metal

TABLE 1. Crystal data, intensity measurements and structure refinement

	Compound 1	Compound 2	Compound 3	Compound 4
Formula	$C_8H_{22}N_2Zn$	$C_8H_{22}N_2Cd$	$C_{16}H_{38}N_2Zn$	$C_{16}H_{38}N_2Cd$
M	211.666	258.687	323.881	370.902
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/a$	*Cmca*	$C2/c$	$C2/c$
a (Å)	13.868(3)	11.196(2)	17.167(5)	17.604(5)
b (Å)	11.616(2)	12.179(2)	9.369(3)	9.484(3)
c (Å)	7.588(2)	17.969(3)	12.916(3)	12.758(3)
α (°)	90	90	90	90
β (°)	94.83(2)	90	107.83(2)	106.07(2)
γ (°)	90	90	90	90
U (Å^3)	1218.02	2450.18	1977.60	2046.8
Z	4	8	4	4
D_c (g cm^{-1})	1.154	1.402	1.088	1.204
F(000)	456	1056	712	784
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
λ (Å)	0.71069	0.71069	0.71069	0.71069
μ (cm^{-1})	20.22	17.34	12.646	10.565
$\theta_{min/max}$ (°)	1.5, 25	1.5, 25	1.5, 25	1.5, 25
Total no. of reflections	2491	1270	2089	2164
No. of unique reflections	2140	1137	1745	1788
No. of observed reflections ($F_o > 3\sigma(F_o)$)	1196	648	1545	1685
No. of refined parameters	126	59	109	109
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.0000121	0.0000232	0.00001	0.000223
Final R	0.0558	0.0464	0.0364	0.0255
Final R_G	0.0513	0.0498	0.0341	0.0331

alkyl adduct is gently heated under vacuum and dissociates giving the ultra-pure alkyl. This technique has been used in the purification of dimethylcadmium [27] and trimethylindium [28]. The removal of n-type dopants, such as MeI used in the preparation of Me_2Zn may be crucial [25].

(3) Control of homogeneous reaction ("prereaction"), by an as yet unknown mechanism, between the Group 12 and Group 16 sources leading to much improved layer growth quality [29].

In developing precursor chemistry for II–VI materials, a number of adducts have been obtained, the structures of which have been determined crystallographically. In this paper, we report the X-ray crystal structures of the metal alkyl *N,N,N′,N′*-tetramethylethylenediamine (TMED) adducts: $Me_2Zn[Me_2N(CH_2)_2NMe_2]$ (**1**), $Me_2Cd[Me_2N(CH_2)_2NMe_2]$ (**2**), $(Me_3CCH_2)_2Zn[Me_2N(CH_2)_2NMe_2]$ (**3**) and $(Me_3CCH_2)_2Cd[Me_2N(CH_2)_2NMe_2]$ (**4**), providing the first structural information for adducts of dimethylcadmium and allowing a direct comparison of coordination spheres in complexes of cadmium and zinc. Two of these compounds have been used successfully in MOCVD, **1** as a p-type dopant for GaAs and the parent alkyl of **4**, bisneopentylcadmium, for the growth of CdS.

2. Experimental details

Samples of the parent alkyls and adducts were prepared as described in the literature [4,30,31]. All experiments were performed in an atmosphere of dry, oxygen-free nitrogen (Schlenk line or dry-box). Amines were purchased from Aldrich and zinc and cadmium dimethyls were a gift from Epichem Ltd. ^1H NMR spectra were obtained using Bruker WP80 or WH400 FT spectrometers, infrared spectra were recorded with a Mattson Polaris FTIR instrument with a small quantity of the adduct in a sealed evacuated gas cell at room temperature (close to 20°C).

Diffraction quality crystals were obtained by sublimation **1** and **2** or recrystallisation from (60–80°C) petroleum ether **3** and **4** at −25°C and sealed into glass capilleries under a nitrogen atmosphere for data collection. The melting points measured were 60–61°C (**1**), 62–63°C (**2**), 86–87°C (**3**) and 78–79°C (**4**). X-Ray data were collected on a CAD4 diffractometer, at room temperature (close to 20°C) operating in the $\omega/2\theta$ scan mode with graphite monochromated Mo Kα radiation as described previously [32]. The structures were solved *via* standard heavy-atom procedures and refined using full matrix least-squares methods [33] with scattering factors calculated using data from ref. 34. All non-hydrogen atoms were refined with anisotropic displacement factors. Crystal data and details of the intensity measurements and refinements are given in Table 1, Fractional atomic coordinates are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

TABLE 2. Fractional atomic coordinates ($\times 10^4$) for $Me_2M[Me_2N(CH_2)_2NMe_2]$ (M = Zn, Cd) and $(Me_3CCH_2)_2M(Me_2N(CH_2)_2NMe_2]$ (M = Zn, Cd)

	x	y	z
$Me_2Zn[Me_2N(CH_2)_2NMe_2]$ (**1**)			
Zn(1)	1936(1)	713(1)	980(1)
N(1)	1431(5)	−932(5)	2201(7)
N(2)	3333(4)	143(6)	2530(7)
C(1)	2094(6)	369(7)	−1548(8)
C(2)	1415(6)	2004(6)	2303(10)
C(3)	2283(7)	−1424(9)	3171(13)
C(4)	3112(7)	−882(9)	3425(13)
C(11)	1047(7)	−1764(8)	937(11)
C(12)	685(7)	−721(8)	3411(12)
C(21)	4110(6)	−78(9)	1427(10)
C(22)	3666(7)	1008(9)	3833(11)
$Me_2Cd[Me_2N(CH_2)_2NMe_2]$ (**2**)			
Cd(1)	5000 [a]	4355(1)	8795(1)
N(1)	5000 [a]	2289(11)	9426(6)
N(2)	5000 [a]	2745(11)	7779(6)
C(1)	3245(8)	4791(10)	8835(6)
C(2)	4011(11)	2190(11)	9892(7)
C(3)	5000 [a]	1369(14)	8847(10)
C(4)	4071(14)	2867(16)	7285(7)
C(5)	4516(20)	1662(20)	8127(11)
$(Me_3CCH_2)_2Zn[Me_2N(CH_2)_2NMe_2]$ (**3**)			
Zn(1)	0 [a]	779(1)	2500 [a]
N(1)	268(2)	2789(2)	3724(2)
C(1)	1086(2)	196(3)	2367(2)
C(2)	1613(2)	−968(3)	3089(3)
C(3)	−128(2)	3994(3)	3055(2)
C(11)	−148(2)	2586(4)	4549(3)
C(12)	1129(2)	3084(4)	4285(3)
C(21)	1169(2)	−2380(3)	2936(3)
C(22)	1829(3)	−545(4)	4285(3)
C(23)	2407(2)	−1162(4)	2815(4)
$(Me_3CCH_2)_2Cd[Me_2N(CH_2)_2NMe_2]$ (**4**)			
Cd(1)	0 [a]	540(1)	2500 [a]
N(1)	259(1)	2805(2)	3755(2)
C(1)	1166(2)	90(3)	2341(2)
C(2)	1675(2)	−1048(3)	3085(2)
C(3)	−125(2)	3961(3)	3023(3)
C(11)	−158(2)	2601(4)	4590(2)
C(12)	1095(2)	3100(4)	4316(3)
C(21)	1250(2)	−2445(3)	2933(3)
C(22)	1847(3)	−598(4)	4286(4)
C(23)	2467(2)	−1221(6)	2842(5)

[a] Invariant position.

Crystals of **1** and **2** were not of good quality and much effort was expended, unsuccessfully, to obtain better. In both cases there is high thermal motion or disorder (or both) and this has adversely affected the accuracy of the structures determined. In particular, there seems to be flexibility of the conformation of the chelating diamine. In compound **2**, it was possible to identify two sites for one of the ethylene carbons but only one for the second which, not unnaturally then shows high displacement factor coefficients. In the case of compound **1**, the motion/disorder affecting the ethylene bridge seems to be continuous and no splitting of peaks occurred. However, because of the motion/disorder, the C–C distance (C(3)–C(4)) is artificially shortened. Attempts to represent each carbon site by two half-atoms near the extremities of the ellipsoids, with constrained "normal" N–C and C–C bond lengths, were not successful.

3. Results and discussions

The structures of **1**, **2**, **3** and **4** as determined by X-ray crystallography are shown in Figs. 1 and 2, and important bond lengths and angles are summarized in Table 3. The structures are all based on discrete molecular units [R_2–M–TMED] with distorted tetrahedral coordination at the metal ion centre; there are no unusually short interactions between adjacent molecules. The bite angle of the TMED determines the coordination of the two nitrogen atoms at the metal atoms with N–M–N (79.8(3)° (**1**) and 77.3(2)° (**3**) for zinc and 71.5(5)° (**2**) and 71.2(2)° (**4**) for cadmium).

The two methyl (**1** and **2**) complexes crystallize in different space groups. Compound **2** lies on a crystallographic mirror plane. We have no evidence that either of the compounds is polymorphic but this possibility cannot be ruled out. The coordination spheres of the two methyls are therefore not strictly comparable as the secondary environment is subtly different for each compound. Dimethylzinc, as characterized in the vapour phase by electron diffraction [35] (M–C 1.930 Å) and rotational Raman spectroscopy [36] (M–C 1.927 Å), is linear as is dimethylcadmium [36] (M–C 2.112 Å, 60°C) by Raman spectroscopy. On interaction with the amine, the linear metal-alkyl unit distorts by 44.2(3)° for zinc (**1**) and 26.0(3)° for cadmium (**3**). There is a small increase in the metal carbon separation accompanying this distortion to (1.989(9), 1.974(9) Å) 1.982(9)(av) for zinc, and for cadmium, the M–C bond length (2.194(12) Å) probably represents a small displacement from the equilibrium bond length of the dialkyl at room temperature. The difference in average bond lengths (0.212 Å) is in line with the difference in covalent radii for zinc and cadmium (1.20 Å and 1.41 Å, respectively). The contacts to the nitrogen atoms at 2.269(8)(av) and 2.571(14)(av) Å for Zn and Cd, respectively, are within the relevant sums of van der Waals radii (2.90 Å for Zn and 3.10 Å for Cd) but indicate only a weak interaction between the metal ion and the nitrogen atom.

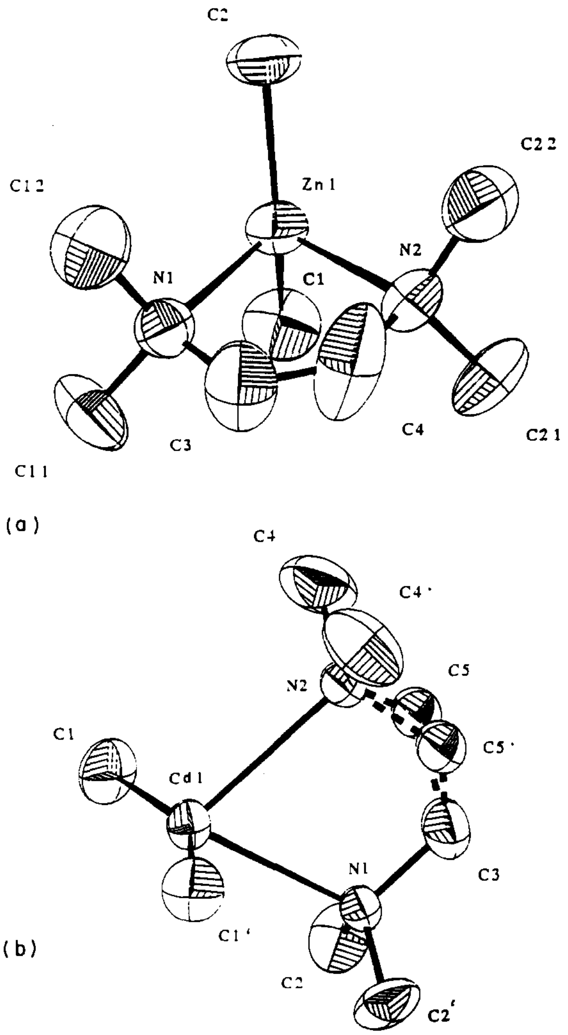

Fig. 1. ORTEP (50% probability) drawing for $Me_2M[Me_2N(CH_2)_2NMe_2]$ showing atom numbering scheme for both Zn (a) and Cd (b) (hydrogen atoms have been omitted).

The two neopentyl complexes (**3** and **4**) are isostructural, with crystallographically imposed C_2 symmetry at the metal centre, and for these compounds a direct comparison can be made between the bond lengths and angles at zinc and cadmium. The coordination of the TMED ligand is potentially limited by both the poorer acceptor properties of the cadmium centre and its size. The effects of coordination on the C–M–C framework are, as would be expected, more pronounced for zinc C–M–C (148(5)°), M–C (2.000(5) Å), as compared to cadmium C–M–C (157(8)°) M–C (2.160(4) Å). The increase in the M–C bond length between the zinc (**3**) and cadmium (**4**) compounds

TABLE 3. Selected bond distances (Å) and angles (°) for $Me_2M[Me_2N(CH_2)_2NMe_2]$ (M = Zn, Cd) and $(Me_3CCH_2)_2M[Me_2N(CH_2)_2NMe_2]$ (M = Zn, Cd)

$Me_2Zn[Me_2N(CH_2)_2NMe_2]$ (1)			
N(1)–Zn(1)	2.260(8)	N(2)–Zn(1)	2.278(8)
C(1)–Zn(1)	1.989(9)	C(2)–Zn(1)	1.974(9)
C(3)–N(1)	1.456(10)	C(11)–N(1)	1.433(9)
C(12)–N(1)	1.460(9)	C(4)–N(2)	1.417(11)
C(21)–N(2)	1.441(9)	C(22)–N(2)	1.457(10)
C(4)–C(3)	1.310(11)		
N(2)–Zn(1)–N(1)	79.8(3)	C(1)–Zn(1)–N(1)	106.7(4)
C(1)–Zn(1)–N(2)	106.4(4)	C(2)–Zn(1)–N(1)	107.1(4)
C(2)–Zn(1)–N(2)	106.9(4)	C(2)–Zn(1)–C(1)	135.8(3)
C(3)–N(1)–Zn(1)	105.8(6)	C(11)–N(1)–Zn(1)	114.0(5)
C(11)–N(1)–C(3)	108.3(8)	C(12)–N(1)–Zn(1)	112.1(6)
C(12)–N(1)–C(3)	109.6(8)	C(12)–N(1)–C(11)	106.9(8)
C(4)–N(2)–Zn(1)	106.4(6)	C(21)–N(2)–Zn(1)	113.4(6)
C(21)–N(2)–C(4)	109.3(8)	C(22)–N(2)–Zn(1)	110.9(6)
C(22)–N(2)–C(4)	108.9(8)	C(22)–N(2)–C(21)	107.9(8)
C(4)–C(3)–N(1)	123.4(9)	C(3)–C(4)–N(2)	123.7(9)
$Me_2Cd[Me_2N(CH_2)_2NMe_2]$ (2)			
N(1)–Cd(1)	2.576(14)	N(2)–Cd(1)	2.566(14)
C(1)–Cd(1)	2.194(12)	C(2)–N(1)	1.470(13)
C(3)–N(1)	1.464(18)	C(4)–N(2)	1.444(15)
C(5)–N(2)	1.486(23)	C(5)–C(3)	1.459(23)
N(2)–Cd(1)–N(1)	71.5(5)	C(1)–Cd(1)–N(1)	100.7(4)
C(1)–Cd(1)–N(2)	100.3(4)	C(1)–Cd(1)–C(1a)	154.0(3)
C(2)–N(1)–Cd(1)	108.5(8)	C(3)–N(1)–Cd(1)	108.5(9)
C(3)–N(1)–C(2)	110.6(9)	C(4)–N(2)–Cd(1)	111.8(9)
C(5)–N(2)–Cd(1)	105.9(10)	C(5)–N(2)–C(4)	91.4(13)
C(2)–N(1)–C(2a)	110.0(13)	C(5)–C(3)–N(1)	118.2(15)
C(4)–N(2)–C(4a)	103.1(15)	C(3)–C(5)–N(2)	113.3(18)
$(Me_3CCH_2)_2Zn[Me_2N(CH_2)_2NMe_2]$ (3)			
N(1)–Zn(1)	2.411(4)	C(1)–Zn(1)	2.000(5)
C(3)–N(1)	1.457(4)	C(11)–N(1)	1.465(4)
C(12)–N(1)	1.459(5)	C(2)–C(1)	1.536(6)
C(21)–C(2)	1.509(6)	C(22)–C(2)	1.526(6)
C(23)–C(2)	1.520(6)	C(3)–C(3a)	1.621(7)
C(1)–Zn(1)–N(1)	105.9(2)	C(3)–N(1)–Zn(1)	104.8(3)
C(11)–N(1)–Zn(1)	109.7(3)	C(11)–N(1)–C(3)	106.9(3)
C(12)–N(1)–Zn(1)	115.7(3)	C(12)–N(1)–C(3)	111.4(4)
C(12)–N(1)–C(11)	108.0(3)	N(1)–Zn(1)–N(1)	77.3(2)
C(2)–C(1)–Zn(1)	122.2(3)	C(21)–C(2)–C(1)	111.3(3)
C(22)–C(2)–C(1)	110.2(3)	C(22)–C(2)–C(21)	108.5(4)
C(23)–C(2)–C(1)	110.3(4)	C(23)–C(2)–C(21)	108.5(4)
C(23)–C(2)–C(22)	108.0(4)		
$(Me_3CCH_2)_2Cd[Me_2N(CH_2)_2NMe_2]$ (4)			
N(1)–Cd(1)	2.642(5)	C(1)–Cd(1)	2.160(4)
C(3)–N(1)	1.477(5)	C(11)–N(1)	1.464(4)
C(12)–N(1)	1.475(5)	C(2)–C(1)	1.548(6)
C(21)–C(2)	1.508(7)	C(22)–C(2)	1.539(7)
C(23)–C(2)	1.518(6)	C(3)–C(3a)	1.517(8)
C(1)–Cd(1)–N(1)	102.0(2)	C(3)–N(1)–Cd(1)	104.4(3)
C(11)–N(1)–Cd(1)	107.3(3)	C(11)–N(1)–C(3)	108.9(3)
C(12)–N(1)–Cd(1)	115.4(3)	C(12)–N(1)–C(3)	112.7(4)
C(12)–N(1)–C(11)	107.8(3)	N(1)–Cd(1)–N(1)	71.2(2)
C(2)–C(1)–Cd(1)	119.0(3)	C(21)–C(2)–C(1)	110.5(3)
C(22)–C(2)–C(1)	109.8(3)	C(22)–C(2)–C(21)	109.0(4)
C(23)–C(2)–C(1)	111.0(4)	C(23)–C(2)–C(21)	109.3(4)
C(23)–C(2)–C(22)	107.2(4)		

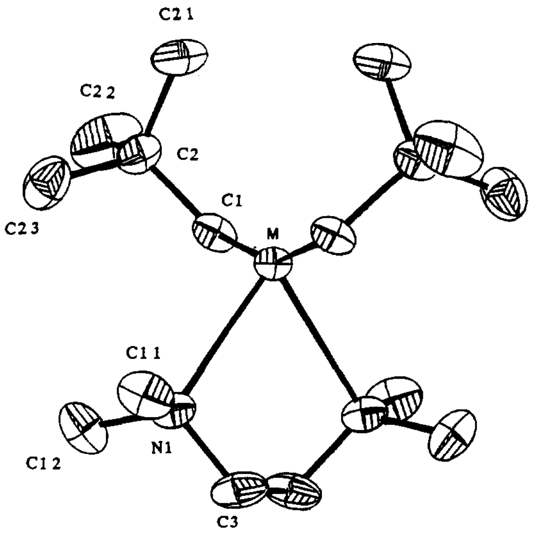

Fig. 2. ORTEP (30% probability) drawing for $(Me_3CCH_2)_2M[Me_2N(CH_2)_2NMe_2]$ (M = Zn, Cd), showing atom numbering scheme (hydrogen atoms have been omitted).

again corresponds reasonably closely to that expected on the basis of the covalent radii (0.21 Å) (*vide supra*).

The metal–nitrogen bond in the dimethylzinc adduct is shorter than in the corresponding neopentyl by 0.142(7) Å. This observation may be rationalized in terms of the slightly stronger σ-donation in the higher alkyl resulting in reduced Lewis acidity at the zinc atom, however, the increased size of the neopentyl group may also play a part in restricting the approach of the TMED. Studies of the electronic spectra of complexes with π-acceptor ligands such as 2,2′-bipyridyl, support the importance of an electronic effect [6] (π for such ligands), suggesting that an electronic effect(σ) may plausibly have some importance for the present compounds. Similarly, for the cadmium alkyls, the M–N bond in the neopentyl (**4**) is 0.071(9) Å longer than that in the methyl (**2**).

The distortions of the C–M–C bond angle may reflect similar electronic effects in that the cadmium centres are less distorted than the zinc centres, cadmium forming a stronger, or at least more covalent bond to the alkyl [29]. The distortions are also smaller in the neopentyls than the methyls, *i.e.* for the strong σ-donors.

3.1. Infrared spectroscopy

The interaction of TMED with the metal centre has also been studied by infrared spectroscopy. The parent methyls are highly reactive liquids with very low degrees of association, their infrared spectra are known [37] and we have not attempted to reinvestigate the spectra. Both bisneopentycadmium and the TMED adduct are modestly stable solids and spectra have been recorded as mineral oil mulls. The M–C stretch in the parent alkyl has been tentatively identified at 568 cm^{-1}; the degree of association in this solid is uncertain. In the TMED adduct, this band has shifted to lower energy (565 cm^{-1}), consistent with the lengthening of the M–C bond (Table 4). The M–C stretch in the bisneopentylzinc adduct has been tentatively identified at 586 cm^{-1}.

The relatively weak metal–nitrogen interaction, in all four complexes, is also indicated by the gas-phase infrared spectra of the vapour above the adducts. Such spectra show that, in all cases, the ligand and the parent dialkyl species are close to completely dissociated in the vapour phase. The majority of the dimethylzinc and dimethylcadmium adducts we have studied are fully dissociated [38]. Electron diffraction studies of the trimethylamine adduct of dimethyl zinc support this suggestion [39].

3.2. NMR spectroscopy

It is also possible to compare the structural results for the complexes with the corresponding solution (be-

TABLE 4. Important bond lengths (Å) and angles (°) in some adducts of Group 12 alkyls and related compounds

	M–C	M–N	C–M–C	N–M–N
Me_2Zn [35,36]	1.930		180.0	
$Me_2Zn[(CH_2NMe)_3]_2$ [8]	1.987	2.410	145.1	105.6
$Me_2Zn[Me_2N(CH_2)_2NMe_2]$ (**1**)	1.982(9) [a]	2.269(8) [a]	135.8(3)	79.8(3)
$[Me_2N(CH_2)_3]_2Zn$ [10]	1.984	2.307	156.4	109.7
by electron diffraction	1.991	2.392	152	117
$(Me_3CCH_2)_2Zn[Me_2N(CH_2)_2NMe_2]$ (**3**)	2.000(5)	2.411(4)	148.3(5)	77.3(2)
Me_2Cd [36]	2.112		180.0	
$Me_2Cd[Me_2N(CH_2)_2NMe_2]$ (**2**)	2.194(12)	2.571(14) [a]	154.0(3)	71.5(5)
by electron diffraction [41]	2.12(2)	2.47(5)	132(11)	84(3)
$(Me_3CCH_2)_2Cd[Me_2N(CH_2)_2NMe_2]$ (**4**)	2.160(4)	2.642(5)	157.0(6)	71.2(2)

[a] Average values.

nzene-d_6) ^{1}H NMR spectra. The stronger interaction of the ligand with **3** as opposed to **4** can be seen by comparing the signals from the methylene protons in both the adduct and parent alkyl. A downfield shift of 0.35 ppm is observed for bisneopentylzinc (δ 0.32 ppm, $(CH_3)_3CCH_2Zn$) on complexation, whereas only a very small shift (< 0.1 ppm) is observed for the corresponding cadmium compound (δ 0.72 ppm, $(CH_3)_3CCH_2Cd$). The signal from the t-butyl groups, however, occurs at 1.33 ppm for both compounds, the effect of the metal being smaller at this position. Similar effects are observed for methyl protons of **1** and **2**.

4. Conclusions

The work presented in the present paper significantly increases our knowledge of the structural chemistry of TMED adducts of divalent metal alkyls. The structures for the cadmium complexes are among the first for such compounds [40]. The fact that the two neopentyls are isomorphous allows a direct comparison of the bonding in the zinc and cadmium complexes. A very recent electron diffraction study of the TMED adduct of dimethyl cadmium [41] allows a comparison of bonding in the vapour phase and solid state for this compound (Table 4).

For zinc, there are now a number of adducts and related compounds with which the coordination geometry at zinc in the present compound can be compared. Bond lengths and angles for the parent alkyls, the chelate bis(3-(dimethylamino)-propyl)zinc $[Zn((CH_2)_3N(CH_3)_2)_2]$ and the recently reported zinc triazine adduct $[(CH_3)_2Zn\{(CH_2NCH_3)_3\}_2]$ are given in Table 4 to allow easy comparison with those for the adduct prepared in the present study. The reported range [10] of Zn–N bond lengths was previously from 1.82 Å in $[Zn(N(SiMe_3)_2)_2]$ to 2.41 Å in $[Zn((CH_2)_3N(CH_3)_2)_2]$ and the bond lengths for the present compounds fall, as expected, towards the upper limit of the range [42].

The compounds have considerable potential for use in the deposition of compound semiconductors by MOCVD. Compound **1** has been used to provide controlled doping for carrier concentrations between 10^{15} and 10^{17} cm^{-3} in GaAs [22]. The other compounds may be useful in similar applications and a study of crystal growth from these compounds is in hand.

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