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Some complexes of neopentylcadmium species with dithio- and di-selenocarbamates: the synthesis, characterization and single crystal X-ray structure of a mixed neopentyl/diethyldiselenocarbamate of cadmium: $[(CH_3)_3CCH_2CdSe_2CNEt_2]_2$

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Abstract

The synthesis and characterization of the neopentyl complexes of cadmium $(CH_3)_3CH_2CCdE_2CNEt_2$ (E = S or Se) and the related mixed metal species $(CH_3)_3CH_2CZn_{0.5}Cd_{0.5}Se_2CNEt_2$ are reported. A single crystal X-ray structure determination on for $(CH_3)_3CH_2CCdSe_2CNEt_2$; the compound is dimeric. All of the complexes decompose to give the corresponding binary or ternary metal chalcogenides.

Key words: Cadmium; Neopentyl; Dithiocarbamate; Diselenocarbamate; Crystal structure

1. Introduction

In a series of recent papers we have systematized the chemistry of compounds containing either dithio- or diseleno-carbamato and alkyl groups bound to either zinc or cadmium [1–4]. For a large number of compounds we have found the structures to be dominated by dimeric species $[RME_2CNR'_2]_2$ [1,3,4], although more recently the use of functionalized thiocarbamates has led to different structural motifs [5,6]. Although we have characterized a mixed metal species $[Me_2ZnCd(Se_2CNEt_2)_2]$ [3] the crystallographic characterization of a simple cadmium complex, has until now eluded us. The present paper reports the synthesis and characterization of cadmium complexes of the stoichiometry $RCdECNEt_2$ (R = neopentyl, $-CCH_2(CH_3)_3$ and E = S (**1**) or Se (**2**)) and a related mixed metal species $RZn_{0.5}Cd_{0.5}E_2CNEt_2$ (**3**).

Compounds of the kind described in the present paper are potentially useful precursors [7] for the deposition of II/VI materials such as zinc selenide or cadmium sulfide by methods such as low pressure metallo-organic chemical vapour phase deposition (LP – MOCVD). Other compounds that can be used to deposit such materials from the vapour phase include thiophosphinates [8,9], simple dithiocarbamates [10,11], and bulky thiolates [12–14].

2. Experimental section

2.1. Chemicals and general methods

Cadmium neopentyl was prepared by the published method [15]. Bisdiethyldiselenocarbamatocadmium(II) was prepared as described previously [3], all other chemicals were from BDH. Solvents were dried, and degassed before use. Air sensitive compounds were handled by use of standard Schlenk/vacuum line and glove box techniques.

2.2. Physical measurements

NMR spectra were recorded using a Bruker AM250 pulsed Fourier transform instrument, infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer as Nujol mulls between KBr plates, and electronic spectra were recorded with a Perkin-Elmer 330 spectrophotometer. Melting points were measured in sealed tubes with an Electrothermal melting point apparatus

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and are uncorrected. Microanalyses were performed at University College London.

2.3. The synthesis of neopentylcadmium-N,N-diethyl-dithio or diseleno-carbamates

In a typical preparation a solution of N,N-diethyldiselenocarbamatocadmium (II) (2.84 g, 4.8 mmol) in toluene (35 ml) was stirred with bisneopentylcadmium (1.22 g, 4.8 mmol) at room temperature for 0.5 h. Concentration of the colourless solution under vacuum gave transparent yellow crystals of neopentylcadmium-N,N-diethyldiselenocarbamate (**2**) (3.77 g, 8.8 mmol, 92%), m.p. 145°C. Neopentylcadmiumdiethyldithiocarbamate (**2**) was prepared by the same method from diethyldithiocarbamatocadmium(II) and bisneopentylcadmium. 89%, m.p. 142–144°C.

2.4. The synthesis of neopentylcadmium-/zincdiethyldithiocarbamate

This mixed complex of cadmium and zinc was prepared by stirring a mixture of 1:1 stoichiometric amounts of N,N-diethyldithiocarbamatozinc(II) and bisneopentylcadmium at room temperature for 20 min and then heating the mixture at 50°C for 10 min. The solvent was removed under vacuum and the product recrystallized from hot toluene to give transparent crystals of neopentylcadmium-/zincdiethyldithio-carbamate (**3**), 90%, m.p. 130°C.

All the compounds were characterized by satisfactory elemental analysis and NMR and infrared spectroscopy.

2.5. Characterizations

2.5.1. $Me_3CCH_2CdS_2CNEt_2$ (1)

^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$, 250.1 MHz) δ 3.53 (4H, q, ^3J(H–H = 7.1 Hz, $(\mathrm{CH_3C}H_2)_2\mathrm{N}$), 1.01 (6H, t, ^3J(H–H) = 7.1 Hz, $(\mathrm{C}H_3\mathrm{CH_2})_2\mathrm{N}$), 1.33 (9H, s, $(\mathrm{C}H_3)_3\mathrm{C}$), no signal for Cd–$\mathrm{C}H_2$. ^{13}C NMR ([^{2}H$_6$]C$_6H_6$, 62.9 MHz) δ 203.19 ($C\mathrm{S_2}$), 50.65 ($\mathrm{N}C\mathrm{H_2}$), 36.59 ($\mathrm{C}(C\mathrm{H_3})_3$), 33.41 ($C\mathrm{H_2Cd}$), no signal for ($C(\mathrm{CH_3})_3$, 12.80 ($(C\mathrm{H_3CH_2})_2\mathrm{N}$). IR (major bands and tentative assignments cm^{-1}) 427 (δ(Cd–S)), 562, 673 (δ(Cd–C)), 984 (δ(C–S)), 1492 (δ(C–N)). Anal. Calc for $\mathrm{C_{10}H_{21}NS_2Cd}$: C, 36.20; H, 6.36; N, 4.22; S, 19.32. Found: C, 36.64; H, 6.47; N, 4.34; S, 19.17%.

2.5.2. $Me_3CCH_2CdSe_2CNEt_2$ (2)

^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$, 250.1 MHz) δ 3.43 (4H, q, ^3J(H–H) = 7.1 Hz, $(\mathrm{C}H_3\mathrm{CH_2})_2\mathrm{N}$), 0.92 (6H, t, ^3J(H–H) = 7.1 Hz, $(\mathrm{C}H_3\mathrm{CH_2})_2\mathrm{N}$), 1.35 (9H, s, $((\mathrm{C}H_3)_3\mathrm{C})$, no signal for $\mathrm{C}H_2\mathrm{Cd}$. ^{13}C NMR ([^{2}H$_6$]C$_6$H$_6$, 62.9 MHz) δ 182.23 ($C\mathrm{Se_2}$), 51.59 ($C\mathrm{H_2N}$), 36.53 ($((C\mathrm{H_3})_3\mathrm{C})$, 33.57 ($C\mathrm{H_2Cd}$), no signal for $C(\mathrm{CH_3})_3$, 12.49 ($(C\mathrm{H_3CH_2})_2\mathrm{N}$). IR (major bands and tentative assignments cm^{-1}) 429 (δ(Cd–Se)), 566, 669 (δ(Cd–C)), 846 (δ(C–Se)), 1496 (δ(C–N)). Anal. Calc for $\mathrm{C_{10}H_{21}NSe_2Cd}$: C, 28.23; H, 4.97; N, 3.29. Found: C, 28.46; H, 5.06; N, 3.52%.

2.5.3. Me_3CCH_2Cd/ZnS_2CNEt_2 (3)

^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$, 250.1 MHz) δ 3.44 (4H, q, ^3J(H–H) = 7.1 Hz, $(\mathrm{CH_3C}H_2)_2\mathrm{N}$), 0.89 (6H, t, ^3J(H–H) = 7.1 Hz, $(\mathrm{C}H_3\mathrm{CH_2})_2\mathrm{N}$), 1.32 (9H, s, $((\mathrm{C}H_3)_3\mathrm{C})$, no signal for $C\mathrm{H_2Cd}$. ^{13}C NMR ([^{2}H$_6$]C$_6$H$_6$, 62.9 MHz) δ 202.56 ($C\mathrm{S_2}$), 50.17 ($C\mathrm{H_2N}$), 36.45 ($((C\mathrm{H_3})_3\mathrm{C})$, 33.29 ($C\mathrm{H_2M}$), no signal for $C(\mathrm{CH_3})_3$, 12.72 ($(C\mathrm{H_3CH_2})_2\mathrm{N}$). IR (major bands and tentative assignments cm^{-1}) 417, 427 (δ(M–S)), 560, 572, 674 (δ(M–C)), 987 (δ(C–S)), 1492 (δ(C–N)). Anal. Calc for $\mathrm{C_{20}H_{42}N_2S_4CdZn}$: C, 38.92; H, 6.86; N, 4.54; S, 20.77. Found: C, 39.23; H, 6.93; N, 4.67; S, 21.03%.

2.6. Crystallography

The structure of **2** was determined by a single crystal X-ray diffraction study of a capillary-mounted sample. Data were collected on an Enraf-Nonius CAD4 diffractometer operating in $\omega/2\theta$ scan mode using graphite monochromated Mo Kα radiation as described previously [16]. The structure was solved in the triclinic space group $P\bar{1}$ (no. 2) using Patterson vector density methods to locate the first Cd position. Refinement proceeded by full-matrix least squares methods using SHELX-76 [17], with scattering factors for neutral atoms assumed [18]. Difference Fourier techniques revealed two Se positions. The solution appeared to involve two dimeric molecules per unit cell with half of each molecule in the asymmetric unit. One of the molecules developed successfully using difference Fourier techniques (Fig. 1). However, the core of the second molecule was clearly disordered, as evidenced by a number of relatively intense peaks with short inter-peak contacts in the difference Fourier map. Assignment of these peaks was made on the basis of two discrete molecular cores, labelled A and B, each with half site occupancy (Fig. 2). The short Cd(2A)–Cd(2B), Se(3A)–Se(4B) and Se(4A)–Se(3B) contacts preclude the simultaneous occupancy of A and B sites in a single molecular core. The positions of the neopentyl groups and the amine part of the diselenocarbamate were unaffected by the disorder and satisfactory refinement was achieved in ordered positions. Assuming a local ordering of either A or B sites in the core of the second molecule, bond lengths and angles are comparable between the two molecules in the asymmetric unit. Hydrogen atoms were not located, for all other atoms anisotropic thermal parameters were refined. Crystal data and details of the intensity measurements

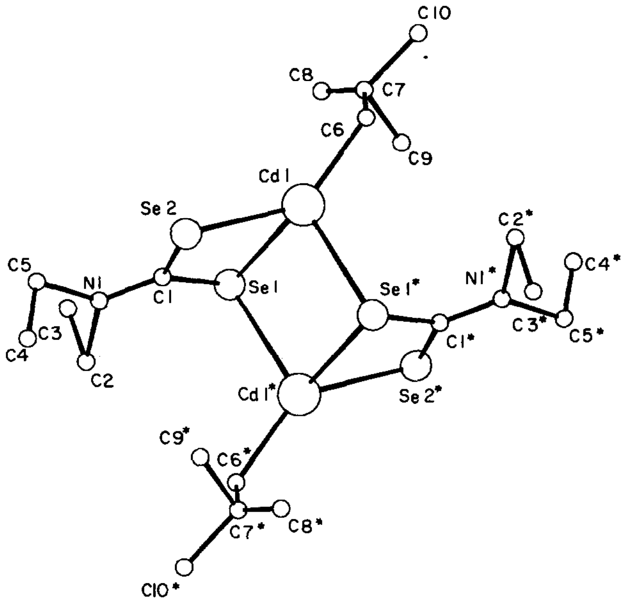

Fig. 1. Structure of $[(CH_3)_3CCH_2CdSe_2CNEt_2]_2$.

and refinement are given in Table 1 with positional parameters in Table 2. Full lists of bond lengths and angles, and lists of anisotropic displacement factor coefficients have been departed at the Cambridge Crystallographic Data Centre.

TABLE 1. Crystal data, Intensity measurements and structure refinement

Formula	$Cd_2Se_4N_2C_{20}H_{42}$
M	851.208
Crystal system	Triclinic
Space group	P_{-1}
a (Å)	9.854(1)
b (Å)	12.653(2)
c (Å)	13.384(2)
α (°)	95.29(1)
β (°)	102.01(1)
γ (°)	106.76(2)
U (Å^3)	1542.11
Z	2
D_c (g cm^{-1})	1.834
$F(000)$	872
radiation	Mo Kα
λ/(Å)	0.71069
μ (cm^{-1})	50.10
$\theta_{min/max}$	1.5, 25°
Total no. of reflections	4652
No. of unique reflections	4270
No. of observed reflections ($F_0 > 3\sigma(F_0)$)	1982
No. of refined parameters	281
Weighting scheme parameter g in $\omega = 1/[\sigma^2(F) + gF^2]$	0.000100
Final R	0.0923
Final R_G	0.0713

3. Results and discussion

Noltes first demonstrated that mixed alkyldithiocarbamates could be synthesized [19] by insertion of CE_2 into mixed alky/alkylamides of zinc. However, this area of synthetic chemistry had lain fallow until the revival of interest in such compounds because of their potential as precursors for II/VI materials. Our preferred synthetic route to such compounds is now the straightforward comproportionation reaction:

$$R_2M + M(E_2CNEt_2)_2 \rightarrow [RCdE_2CNEt_2]_2$$

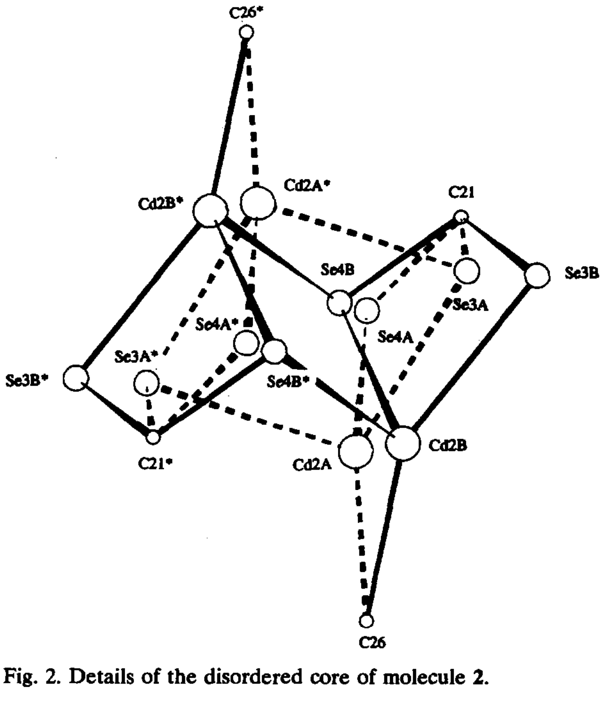

Fig. 2. Details of the disordered core of molecule 2.

The present compounds of stoichiometry $RCdE_2CNEt_2$ (R = neopentyl, $-CCH_2(CH_3)_3$ and E = S (1) or Se (2)) and $RZn_{0.5}Cd_{0.5}E_2CNEt_2$ (3) complete our structural survey of the compounds formed with simple alkyls and dichalcogenocarbamato functions. All were prepared in high yield by the appropriate comproportionation reaction, and are air sensitive compounds which can be recrystallized from hot benzene or toluene. The compounds show no unexpected features in their infra-red or nmr spectra when compared with data from our earlier studies of related compounds.

The main features of the NMR spectra are as follows. The ^1H NMR spectrum generally shows a quartet and triplet for the N-ethylene protons and a singlet for the methyl protons of the neopentyl group. No signal was observed for the methylene protons of the neopentyl group coordinated to cadmium; such protons

TABLE 2. Fractional atomic co-ordinates (×10000) and equivalent isotropic temperature factors (Å^2 ×1000) for $Cd_2Se_4N_2C_{20}H_{42}$

Atom	x	y	z	U_{eq}
Cd(1)	185(2)	946(2)	6264(1)	91(1)
Cd(2A)	1155(7)	1481(5)	93(11)	93(4)
Cd(2B)	1354(7)	1287(5)	848(11)	97(4)
Se(1)	−1999(3)	176(2)	4407(2)	79(2)
Se(2)	−1782(3)	−885(2)	6488(2)	83(2)
Se(3A)	1959(14)	509(8)	−1426(7)	66(4)
Se(3B)	2745(17)	−195(11)	1111(8)	94(5)
Se(4A)	1860(16)	−347(10)	742(9)	83(5)
Se(4B)	1240(13)	220(9)	−1101(7)	76(4)
N(1)	−4288(27)	−1675(26)	4789(16)	139(19)
N(21)	2882(31)	−1301(24)	−822(16)	122(17)
C(1)	−2884(29)	−914(19)	5168(15)	61(14)
C(2)	−4778(39)	−1914(28)	3616(17)	166(28)
C(3)	−5658(37)	−1108(32)	3632(28)	168(27)
C(4)	−5017(48)	−3456(30)	5206(25)	209(29)
C(5)	−5086(37)	−2290(29)	5521(24)	180(27)
C(6)	1281(43)	2690(28)	7092(26)	187(25)
C(7)	782(80)	3515(33)	6738(31)	182(33)
C(8)	−469(51)	3557(35)	6113(53)	228(33)
C(9)	1350(89)	3562(43)	5795(59)	259(51)
C(10)	1845(45)	4691(29)	7319(29)	205(24)
C(21)	2434(31)	−555(22)	−454(19)	77(16)
C(22)	3108(31)	−1298(28)	−1896(16)	117(22)
C(23)	1780(36)	−2214(22)	−2571(23)	159(26)
C(24)	4406(40)	−1949(39)	267(28)	214(35)
C(25)	2788(40)	−2279(24)	−229(24)	185(33)
C(26)	1303(45)	3110(43)	950(38)	248(37)
C(27)	2597(58)	3929(42)	1186(27)	155(30)
C(28)	2665(62)	5029(32)	1694(43)	268(41)
C(29)	3250(55)	4070(36)	409(33)	261(38)
C(210)	3462(81)	3594(50)	1848(46)	449(63)

are often hard to observe perhaps due to an exchange process [1]. The ^{13}C spectra all show a clear resonance for the methylene carbon, but for these spectra the quaternary carbons are not observed. There are only small chemical shift differences in the ^1H spectra of the various compounds reported in the present study. However the ^{13}C spectra do clearly show the difference between the CS_2 (δ 203.19) and CSe_2 (δ 182.23) carbons.

Spectroscopic studies have lent support to the formulation of cadmium complexes $RCdECNEt_2$ with simple amines and carbamates as dimers $[RCdECNEt_2]_2$ [1,3], and a single crystal X-ray study is now reported in support of this conjecture. Perhaps surprisingly the only other cadmium complex of this kind, structurally defined before this was a polymer derived from dimethyl cadmium and $S_2CN(Me)CH_2CH_2CH_2N(Me)_2$ (the thiocarbamate derived from trimethylpropylenediamine) [6]. We have also recently reported the crystal structure of the parent bisdiethyldiselenocarbamate of cadmium [20].

Although there were some problems in refining the structure of **2**, largely associated with the presence of three heavy atoms in each asymmetric unit (one cadmium atom and two selenium) refinement of the structure was thought to be worthwhile in order to complete the series. Work on the corresponding sulphur complex **1** was hampered by the poor quality of the crystals of all the samples prepared to date.

Within the constraints of the present determination the structure of **2** has no unusual features. Each cadmium is four-coordinate and bound to three selenium atoms and one carbon. The overall molecular structure is dimeric (Fig. 1), and similar to that observed for the related zinc diethyldithiocarbamate [4]. The structure has no unusual bond lengths or angles. The Cd–Se bond lengths (monodentate) are in the range 2.645(3) Se(2)–Cd(1) to Se(3B)–Cd(2B) 2.63(2) Å which are similar to those in bisdiethyldithiocarbamate [20] 2.65 Å (av). The Cd–C bond length 2.22 Å (av) is close to those observed in other cadmium alkys [21–25].

In preliminary studies compound **(1–3)** have all been shown to decompose under LP-MOCVD conditions to give thin films of the corresponding binary and ternary phases. A comparative study of various mixed alkyl carbamato species as precursors for chalcogenides is at present under way in our laboratory.

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