Sterically Hindered Chalcogenolato Complexes. Mono- and Di-meric Thiolates and Selenolates of Zinc and Cadmium; Structure of $[{Cd(SeC_6H_2Bu^t_3-2,4,6)_2}_2]$, the First Three-coordinate Cadmium-Selenium Complex[†]

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Protolysis of $M[N(SiMe_3)_2]_2$ (M = Zn or Cd) with arenechalcogenols 2,4,6-R₃C₆H₂EH (E = S or Se; R = Me, Prⁱ or Bu^t) gives the corresponding chalcogenolato complexes M(EC₆H₂R₃-2,4,6)₂ in high yield. Complexes with R = Me form co-ordination polymers which are soluble only in strongly coordinating solvents. An adduct [Cd(SC₆H₂Me₃-2,4,6)₂(py)₂] can be isolated which dissociates in vacuo with quantitative loss of pyridine (py). Complexes with R = Pr' readily dissolve in poorly coordinating solvents in which they form oligomers. NMR, infrared and Raman evidence suggests that the sterically more hindered tris-tert-butylbenzenechalcogenolato complexes of zinc and cadmium are dimeric in the solid state but dissociate in hydrocarbon solution to give two-co-ordinate monomers. The compound $Zn(SeC_{6}H_{2}Bu^{t}_{3}-2,4,6)_{2}$ forms a 1:1 adduct with tetrahydrofuran. The structure of [{Cd(SeC₆H₂Bu^t₃-2,4,6)₂}] was determined by X-ray diffraction. The molecule is an asymmetrically bridged dimer, with three-co-ordinate cadmium in a distorted trigonal-planar arrangement. The Cd-Se distances are ca. 0.1 Å shorter than in comparable four-co-ordinate complexes.

The structures of arene-thiolato and -selenolato complexes of zinc and cadmium consist generally of infinite lattices constructed by bridging chalcogenolato ligands in which the metal centres tend to be present as four-co-ordinate ions in a pseudo-tetrahedral co-ordination sphere. Since the aryl substituents have to be accommodated, these structures are sensitive to steric effects, as exemplified by the polyadamantoid cage structures of $[Zn_4(SPh)_8(MeOH)]$,¹ [{Cd(SPh)₂}_n]² and [{Cd(SC₆H₄Me-*p*)₂}_n],² while sterically more hindered *ortho*substituted aryls and the co-ordination of donor molecules produce more open two-dimensional structures.^{2,3} With the exception of bis(pyridinethiolato)cadmium and related S-N complexes, which form linear chains of six-co-ordinate cadmium,⁴ the introduction of strong donor ligands, sometimes coupled with an increased steric bulk of the aryl substituents, prevents the formation of co-ordination polymers and produces mono- and di-meric molecular complexes of the type [M(ER)2- L_2 ⁵ and [{M(ER)(μ -ER)L}₂] (E = S or Se, L = N- or Pdonor ligand).⁶ As part of our search for volatile chalcogenolato complexes of Group 12 metals as one-component precursors for Group 12-16 semiconductor materials we have recently shown that employment of the sterically highly hindered 2,4,6-tertbutylbenzenethiolato ligand produces an unusually low-coordinate homoleptic cadmium complex, $[{Cd(SC_6H_2Bu^t_3 2,4,6)_{2}_{2}$, free of neutral donor ligands, which is dimeric in the solid state but dissociates to give monomers in solution.⁷ Here we report the preparation of a series of homoleptic zinc and cadmium complexes of arene-thiolato and -selenolato ligands of varying degrees of steric hindrance, 2.4.6- $R_3C_6H_2E^-$ (R = Me, $Pr^{i} \text{ or } Bu^{t}; E = S \text{ or } Se).$

Results and Discussion

Although zinc and cadmium complexes of arenechalcogenols are commonly prepared according to equation (1) from a metal

$$MX_2 + 2REH + 2NEt_3 \longrightarrow M(ER)_2 + 2[NEt_3H]X \quad (1)$$

(R = aryl)

salt, the thiol and a tertiary amine as base in a polar solvent, we found this method less suitable for the preparation of complexes with ligands of high steric hindrance. Such complexes are best synthesised by the reaction of the metal bis(trimethylsilyl)amides with the thiol or selenol in a non-co-ordinating solvent, preferably in light petroleum [equation (2)].

$$M[N(SiMe_3)_2]_2 + 2 R \xrightarrow{R} EH \xrightarrow{R} M \begin{bmatrix} R \\ E \xrightarrow{R} \\ R \end{bmatrix}_2 (2)$$

+ 2 HN(SiMe_3)_2
$$M = Zn \text{ or } Cd$$
$$E = S \text{ or } Se$$
$$R = Me, Pr^{i} \text{ or } Bu^{i}$$

Neat 2,4,6-trimethylbenzeneselenol is prepared by the acidification of LiSeC₆H₂Me₃-2,4,6 obtained by treatment of mesityllithium with selenium powder, with aqueous HCl. Some dimesityl diselenide is formed as a by-product. A more generally applicable method for the synthesis of anhydrous selenols is the reduction of the diaryl diselenide with LiBHEt₃ in tetrahydrofuran (thf), followed by acidification with HBF₄·Et₂O in light petroleum (Scheme 1). The conversion is almost quantitative, and the selenol solutions obtained in this way can immediately be used for subsequent reactions.

⁺ Bis[(μ -2,4,6-tri-tert-butylbenzeneselenolato- $\kappa^2 Se$)(2,4,6-tri-tert-butyl benzeneselenolato-ĸSe)cadmium].

Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1991, Issue 1, pp. xviii-xxii.

Non-S.I. unit employed: mmHg \approx 133 Pa.

| Table 1 Proton NMR data for zinc and cadmium chalc | cogenolates, $M(EC_6H_2R_3-2,4,6)_2$ |
|--|--------------------------------------|
|--|--------------------------------------|

| Complex | R | <i>o</i> -R | <i>p</i> -R | Aryl |
|---|-----------------|-----------------|---|---------------|
| $1 \operatorname{Zn}(\operatorname{SR}^1)_2^a$ | Me | 2.62 (s, 6 H) | 2.18 (s, 3 H) | 6.70 (s, 2 H) |
| $2 \operatorname{Zn}(\operatorname{SeR}^{1})_{2}^{a}$ | Me | 2.68 (s, 6 H) | 2.18 (s, 3 H) | 6.77 (s, 2 H) |
| $3 \operatorname{Cd}(\operatorname{SR}^1)_2^a$ | Me | 2.63 (s, 6 H) | 2.13 (s, 3 H) | 6.72 (s, 2 H) |
| $4 \operatorname{Cd}(\operatorname{SeR}^{1})_{2}^{a}$ | Me | 2.68 (s, 6 H) | 2.18 (s, 3 H) | 6.77 (s, 2 H) |
| $6 \operatorname{Cd}(\operatorname{SR}^2)_2^{\overline{b}}$ | Pr ⁱ | 0.81 (d, 12 H) | 1.17 (d, 6 H, CHMe ₂) | 6.69 (s, 2 H) |
| - | | 3.61 (spt, 2 H) | 2.75 (spt, 1 H, $CHMe_2$, J = 7 Hz) | |
| $7 \operatorname{Cd}(\operatorname{SeR}^2)_2^{b}$ | Pr ⁱ | 0.87 (d, 12 H) | 1.11 (d, 6 H, CHMe ₂) | 6.77 (s, 2 H) |
| | | 3.59 (spt, 2 H) | 2.73 (spt, 1 H, $CHMe_2$, J = 7 Hz) | |
| $8 \operatorname{Zn}(\operatorname{SR}^3)_2^b$ | Buʻ | 1.23 (s, 18 H) | 1.04 (s, 9 H) | 6.87 (s, 2 H) |
| 9 $[Zn(SR^3)_2(OEt_2)]^{b,c}$ | But | 1.60 (s, 18 H) | 1.25 (s, 9 H) | 7.40 (s, 2 H) |
| $10 \operatorname{Zn}(\operatorname{SeR}^3)_2^{b}$ | Buʻ | 1.40 (s, 18 H) | 1.14 (s, 9 H) | 7.20 (s, 2 H) |
| 11 $[Zn(SeR^3)_2(thf)]^{b,d}$ | But | 1.50 (s, 18 H) | 1.20 (s, 9 H) | 7.30 (s, 2 H) |
| $12 \operatorname{Cd}(\operatorname{SeR}^3)_2^{b}$ | But | 1.56 (s, 18 H) | 1.28 (s, 9 H) | 7.24 (s, 2 H) |

^a In [²H₅]pyridine solution. ^b In CDCl₃ solution. ^c Co-ordinated Et₂O: δ 1.20 (t, 6 H) and 3.44 (q, 4 H). ^d Co-ordinated thf: δ 1.50 (m, 4 H) and 3.26 (m, 4 H).

 Table 2
 Carbon-13 NMR data for zinc and cadmium chalcogenolates, M(EC₆H₂Bu¹₃-2,4,6)₂*

| Zn(SR ³) ₂ 8 | $\frac{\text{Zn}(\text{SeR}^3)_2}{10}$ | [Zn(SeR ³) ₂ (thf)] 11 | Cd(SR ³) ₂ | $\frac{\text{Cd(SeR}^3)_2}{12}$ | Assignment |
|--|--|--|-----------------------------------|---------------------------------|------------------------|
| 129.1 | | 122.8 | | | ipso-C |
| 153.0 | 153.6 | 153.9 | 152.9 | 153.8 | ortho-C |
| 122.6 | 122.5 | 122.1 | 122.5 | 122.7 | meta-C |
| 148.0 | 148.3 | 147.4 | 147.7 | 148.4 | para-C |
| 38.0 | 38.7 | 38.8 | 38.0 | 38.9 | ortho-CMe3 |
| 32.4 | 32.5 | 32.3 | 32.0 | 32.6 | ortho-CMe ₃ |
| 35.0 | 34.9 | 34.8 | 34.9 | 35.0 | para-CMe ₃ |
| 31.6 | 31.5 | 31.5 | 31.5 | 31.6 | para-CMe ₃ |
| | | 69.7 | | | OCH ₂ (thf) |
| | | 25.3 | | | CH ₂ (thf) |

* In CDCl₃ solution, 22.5 MHz, 28 °C.



Scheme 1 (i) LiBHEt₃, thf, room temperature; (ii) HBF₄·OEt₂, -78 °C

The physical properties and the structures of the complexes are determined by the degree of steric interaction provided by the aryl substituents, and the discussion will therefore be structured according to the ligands employed. NMR spectroscopic data on the complexes are collected in Tables 1 and 2.

Mesityl Complexes, $M(EC_6H_2Me_3-2,4,6)_2$.—The mesityl chalcogenolato complexes $Zn(SR^1)_2$ 1, $Zn(SeR^1)_2$ 2, $Cd(SR^1)_2$ 3 and $Cd(SeR^1)_2$ 4 ($R^1 = C_6H_2Me_3-2,4,6$) are all obtained as polymeric solids which dissolve only in co-ordinating solvents [dimethylformamide (dmf), dimethyl sulphoxide (dmso), pyridine]. Crystals suitable for X-ray diffraction could not be grown. The polymeric nature of compounds of this kind has been elucidated by Dance and co-workers¹⁻³ in the case of sterically less-hindered arenethiolates. Although the PhS complexes of Zn and Cd consist of three-dimensional networks of adamantoid cages, this is not the case if *ortho*-substituents are present on the aromatic ring.³ In view of the recently established one-dimensional polymeric structure of [{Cd(TeC_6H_2Me_3-

 $2,4,6)_{2}_{\infty}$ ⁸ it is probable that mesityl thiolates and selenolates of Zn and Cd also form polymeric chains rather than admantoid cages.

The compound $Cd(SR^1)_2$ forms a crystalline pyridine adduct, $[Cd(SR^1)_2(py)_2]$ 5 which readily loses pyridine on heating *in vacuo* or more slowly on storage at 10 °C. No defined pyridine adduct was obtained with the analogous selenium complex. The compound $Cd(SeR^1)_2$ is significantly more soluble than the SR^1 analogue, although none of these compounds exhibits appreciable volatility.

Tri(isopropyl)phenyl Complexes, Me(EC₆H₂Prⁱ,2,4,6)₂. The reaction of $Cd[N(SiMe_3)_2]_2$ with R²SH gives $Cd(SR^2)_2$ 6 $(R^2 = C_6 H_2 Pr_{3}^{i} - 2, 4, 6)$ as a fine crystalline white solid which is poorly soluble in light petroleum but dissolves in warm toluene. It is monomeric in pyridine and in chloroform solution at room temperature; as in the case of the tri-tert-butylphenyl derivatives described below, only one type of aryl ligands can be discerned by ¹H NMR spectroscopy. On lowering the temperature, ligandexchange processes become apparent, as indicated by a broadening of all proton signals and the loss of a coupling pattern for the $CHMe_2$ groups, before the compound begins to precipitate below -45 °C. The poor solubility of 6 at low temperatures has prevented cooling to a point where a rigid structure is obtained and terminal and bridging thiolate ligands become distinguishable. In contrast to the mesityl derivatives described above, 6 sublimes at 200 °C (0.01 mmHg); the melt decomposes at 300 °C to give polycrystalline CdS. The compound Cd(SeR²)₂ 7 has very similar solubility properties; it sublimes at 230 °C (0.001 mmHg). The variable-temperature proton NMR behaviour of 7 (-45 to +30 °C) is almost identical to that of its thiolato analogue 6.

We have been unable to isolate $Zn(SR^2)_2$ in a pure form; the

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Fig. 1 Fourier-transform Raman spectra of thiolato complexes (a), $Zn(SR^3)_2$ and (b) Cd(SR³)₂. Bands assigned to metal-sulphur vibrational modes are indicated by shading



compound has been mentioned as a reaction intermediate.^{5a,b} The compound $Zn(SeR')_2$, too, could only be obtained as a viscous oil which did not form crystalline adducts with a number of donor ligands.

Tri-tert-butylphenyl Complexes, $M(C_6H_2Bu_3^*-2,4,6)_2$.—The high steric hindrance provided by the 2,4,6-tri-tert-butylphenyl substituent (\mathbb{R}^3) severely restricts the maximum co-ordination number the metal can obtain, an effect that is most strongly felt by an ion of small radius such as zinc. The compound $Zn(SR^3)_2$ 8 is obtained in high yield as a colourless crystalline solid which is highly soluble in chloroform and toluene, but less so in light petroleum. The ¹H NMR spectrum in CDCl₃ is typical of a monomeric complex with a two-co-ordinate metal centre. The only change observed in cooling from 25 to -50 °C is the



Fig. 2 Fourier-transform Raman spectra of selenolato complexes (a) Zn(SeR³)₂ and (b) Cd(SeR³)₂. Shading indicates bands due to metal-selenium vibrational modes

broadening of the signal due to the *ortho-tert*-butyl groups as a consequence of hindered rotation. The compound forms a 1:1 adduct with diethyl ether, $[Zn(SR^3)_2(OEt_2)]$ 9. While this work was in progress this compound was prepared independently and structurally characterised.⁹

The compound $Zn(SeR^3)_2$ 10 is similarly obtained as a white crystalline solid of low solubility in light petroleum or dichloromethane. It decomposes in refluxing toluene to give ZnSe. It forms a very soluble monomeric 1:1 adduct with thf, [Zn(SeR^3)_2(thf)] 11.

The compound Cd(SeR³)₂ 12 is isolated as bright yellow crystals which are sparingly soluble in hexane but are readily recrystallised from warm toluene. A preliminary note on its synthesis has appeared.⁷ The compound sublimes at 240 °C (0.01 mmHg) and decomposes from the vapour phase on the surface of GaAs(100) targets heated to 360 °C to deposit films of CdSe.¹⁰ Like Cd(SR³)₂, the complex is dimeric in the solid state (see below) but, according to variable-temperature NMR spectroscopy, dissociates in benzene or chloroform solution to give two-co-ordinate monomers (Scheme 2). Whereas two-coordinate linear structures are well documented for mercury,¹¹ Cd(SR³)₂⁷ and the zinc and cadmium tri-*tert*-butylbenzenechalcogenolato complexes described here are to our knowledge the first of their class.

Infrared and Raman Spectra.—The Fourier-transform Raman and infrared data in the region relevant for metal– chalcogenide vibrations (600–100 cm⁻¹) of the compounds described here are given in Table 3. Whereas there is no difficulty in identifying the IR bands associated with M–E vibrations (E = S or Se), the Raman spectra contain numerous bands due to the aryl substituents, rendering reliable identification of all M–E modes difficult; a rigorous analysis of the vibrational spectra was therefore not attempted.

As expected for polymeric complexes with bridging chalcogenolate ligands, the M-E stretching modes of 1-4 contain significant bending components and occur at low frequencies ($< 280 \text{ cm}^{-1}$) as somewhat broad, poorly structured bands. The spectra of the oligomeric tri(isopropyl)phenyl complexes 6 and 7 are better resolved and are shifted by *ca*. 50-25 cm⁻¹ to higher frequencies, compared to 2 and 4, respectively.

| Zn(SR ¹) ₂ 1 | $Cd(SR^1)_2$ | Zn(SR ¹) ₂ 2 | $\frac{\mathrm{Cd}(\mathrm{SeR}^1)_2}{4}$ | Cd(SR ²) ₂ 6 | $Cd(SeR^2)_2$ 7 | Zn(SR ³) ₂ 8 | Cd(SR ³) ₂ ⁷ | $\frac{\text{Zn}(\text{SeR}^3)_2}{10}$ | $\frac{\mathrm{Cd}(\mathrm{SeR}^3)_2}{12}$ |
|--|---------------|--|---|--|-----------------|--|--|--|--|
| 626w | 623w | * | 592m | 614vw | * | 608w | 608m | | |
| 573m | 577m | | 566s | 570wm | | 568s | 569m | 570s | 568m |
| 544w | | | 543m | 523w | | 494w | 595w | 485w | 480w |
| | | | | 487wm | (404s) | 415w | 422w | 401w | 398w |
| | | | | 448W | | 393W | | | |
| | | | | 412m | | (101-12) (390s) | | | |
| 405w | 396wm | | | (407m) | | v(M-E) | (361s) | | |
| | | | | () | | · (/ | v(M-E) | | |
| (364m) | | | | | | | (339s) | | |
| | | | | | | | v(M-E) | | |
| 361w | | | 349w | | | 328m | | 331w | 329w |
| 325w | 323w | | 325w | | | | 300m | 303w | |
| (214) | (222) | | | | | | V(M-E) | V(M-E) | |
| (314m) | (322m) | | | | | | (2938) v(M-E) | (29011) $y(M_{-}E)$ | |
| 297w | | | | (293m) | | | 273m | V(IVI-L) | |
| 237.0 | | | | v(M-E) | | | 2,011 | | |
| | | | | 285s (sh) | | | 258m | 260s | 258m |
| | | | | v(M-E) | | | | | |
| (273s) | | | | 279s | | 255s | | | (257m) |
| v(M–E) | | | | ν(M-E) | | v(M–E) | | (222) | v(M-E) |
| | | | | | | | | (230m) | (222s) |
| 267 | | (260) | 260- | (266a) | | | | V(M-E) | V(M-E) |
| 207W 240w | (2480) | (200W) | 200111 | (2008) | | | | 229 III $y(\mathbf{M}_{-}\mathbf{F})$ | $\nu(M-F)$ |
| 240 | v(M-E) | | | | (205s) | | | V(IVI-L) | V(IM-L) |
| (226m) | (228m) | | | | v(M-E) | 194w | 181w | 197vw | |
| v(M-E) | v(M-E) | | | | . (| | v(M-E) | | |
| | 222w | | 217wm | | | 139s | 141m | 143s | 145s |
| | | | v(M-E) | | | ν(M–E) | | | |
| | (210m) | (210s) | (203m) | | | 120w (sh) | 118w | 118s | 97m |
| | v(M-E) | ν(M-E) | 102 | | | | | v(M-E) | |
| | | | 193m | | | | | | |
| | | | (180s) | 180m | | | | | |
| | | | v(M-E) | 100111 | | | | | |
| 151s | | | 159w | 143m | | | | | |
| v(M-E) | | | | | | | | | |
| 140s | 130s | | | | | | | | |
| ν(M-E) | v(M–E) | | | | | | | | |
| 121m | | | 116vs | 98vs | | | | | |
| | | | V(M−E) | | | | | | |
| * No Raman | spectrum reco | rded due to flu | lorescence. | | | | | | |

Table 3 Raman and infrared data (cm⁻¹) for zinc and cadmium chalcogenolates in the region 630-100 cm⁻¹. Infrared data in parentheses

The Raman spectra of the sterically highly hindered tri-*tert*butylphenyl complexes are shown in Figs. 1 and 2. The compound $Zn(SR^3)_2$ 8 gives rise to a single IR-active Zn-S stretching band at 390 cm⁻¹, *ca.* 120 cm⁻¹ higher than for compound 1. While the simplicity of the IR spectrum could be taken to suggest a linear monomeric molecule, the Raman spectrum possesses three bands with v(Zn-S) character, a weak band at 393 cm⁻¹ and two stronger bands at 255 and 139 cm⁻¹, indicative of an asymmetrically bridged dimeric structure similar to that of the analogous cadmium complexes.

The cadmium complex $Cd(SR^3)_2$ is included here for comparison. The IR spectrum exhibits two strong bands at 361 and 339 cm⁻¹ and a weaker feature at 295 cm⁻¹, as expected for a compound with three Cd–S bonds of different length. Two Cd–S bands can be identified in the Raman spectrum, at 300 and 181 cm⁻¹; in addition, two aryl bands at 273 and 258 cm⁻¹ are unusually strong and may overlap with a further Cd–S band.

For the selenolato complex 10, three Raman-active Zn–Se bands (303, 229 and 118 cm⁻¹) and one IR band (296 cm⁻¹) are found; a weaker IR band at 230 cm⁻¹ is most likely due to a ligand vibration. Again, a dimeric structure is suggested. Compound 12 shows two IR bands at 257 and 222 cm⁻¹, while only one Raman band can be assigned with certainty (215 cm⁻¹).

These results confirm the presence of terminal as well as

bridging chalcogenolate ligands and underline the trend, confirmed by X-ray diffraction studies, that a reduction in the degree of association through steric hindrance strengthens the M-E bond; this is particularly noticeable in the case of zinc.

Structure of $[{Cd(SeR^3)_2}_2]$ 12.—The structure of compound 12 is shown in Fig. 3, and bonding and positional parameters are given in Tables 4 and 5.

The compound exists in the solid state as an asymmetrically bridged dimer. It is isostructural to $Cd(SR^3)_2$.⁷ The Cd_2Se_2 ring forms a planar parellelogram. The difference between the two Cd–Se distances within the ring [Cd(1)–Se(1*) – Cd(1)–Se(1)] is 0.09 Å, slightly larger than in the sulphur analogue (0.08 Å). Whereas the bridging selenium atoms are distinctly pyramidal, the co-ordination geometry of cadmium is close to trigonal planar (sums of angles: 335.7 and 358.3° for Se and Cd, respectively). Since the Se(1)–Cd(1)–Se(1*) angle is compressed to 85.9°, the exocyclic Se_{term}–Cd–Se_{br} angles exceed 120° but are very similar (134.3 and 138.1°). Three-co-ordinate selenium complexes of cadmium or other divalent metals have to our knowledge not been observed previously.

The terminal selenium–cadmium bond [2.483(3) Å] is considerably shorter than the two metal–selenium distances within the ring; the bond length differences are 0.116 and 0.21 Å.



Fig. 3 Molecular structure of $[{Cd(SeR^3)_2}_2]$ 12, showing the atomic numbering scheme

| Table 4 | Bond | lengths | (Å) | and | angles | (°) | for | $[{Cd(SeC_6H_2Bu_3^{t}-$ |
|-----------------|------|---------|-----|-----|--------|-----|-----|--------------------------|
| $2,4,6)_2\}_2]$ | | | | | | | | |

| Se(1)-Cd(1) | 2.599(4) | Se(2)-Cd(1) | 2.483(3) |
|-----------------------|-----------|-----------------------|-----------|
| Se(1)-Cd(1*) | 2.693(3) | C(1)-Se(2) | 1.956(8) |
| C(19)-Se(1) | 1.961(8) | C(14)-C(1) | 1.418(11) |
| C(2)-C(1) | 1.406(11) | C(7)-C(2) | 1.388(10) |
| C(3)-C(2) | 1.574(12) | C(8)-C(7) | 1.367(10) |
| C(9)-C(8) | 1.557(11) | C(13)-C(8) | 1.388(10) |
| C(15)-C(14) | 1.560(12) | C(14)-C(13) | 1.383(10) |
| Se(2)-Cd(1)-Se(1) | 134.3(3) | C(19)-Se(1)-Cd(1) | 111.7(3) |
| $Se(1)-Cd(1)-Se(1^*)$ | 85.9(3) | $Cd(1)-Se(1)-Cd(1^*)$ | 94.2(3) |
| $Se(2)-Cd(1)-Se(1^*)$ | 138.1(3) | $C(19)-Se(1)-Cd(1^*)$ | 129.8(3) |
| C(1)-Se(2)-Cd(1) | 95.8(3) | C(2)-C(1)-Se(2) | 120.2(6) |
| C(14)-C(1)-Se(2) | 119.5(6) | C(14)-C(1)-C(2) | 120.0(7) |
| C(3)-C(2)-C(1) | 125.1(7) | C(7)-C(2)-C(1) | 117.7(7) |
| C(7)-C(2)-C(3) | 117.1(7) | C(8)-C(7)-C(2) | 123.0(7) |
| C(9)-C(8)-C(7) | 122.1(7) | C(13)-C(8)-C(7) | 117.8(7) |
| C(13)-C(8)-C(9) | 120.0(7) | C(14)-C(13)-C(8) | 122.6(8) |
| C(13)-C(14)-C(1) | 117.6(7) | C(15)-C(14)-C(1) | 124.5(7) |
| C(15)-C(14)-C(13) | 117.8(7) | C(20)-C(19)-Se(1) | 116.5(6) |
| C(32)-C(19)-Se(1) | 122.3(5) | C(32)-C(19)-C(20) | 121.1(6) |
| | | | |

Such a bond-length distribution between bridging and terminal ligands is not uncommon, and differences of a similar order of magnitude have been observed in four-co-ordinate cadmium benzeneselenolates, e.g. in $[{Cd_2(\mu-SePh)_2(SePh)_2L}_{\infty}]$ (L = $Et_2PC_2H_4PEt_2$) (2.678 and 2.564 Å)^{6b} and in the cluster anion $[cd_8(\mu-S)(\mu-SePh)_12(SePh)_4]^{2-}$ (bridging 2.638, 2.69 Å; terminal 2.572 Å).^{12.*} A comparison of these values with those of **12** indicates that both bridging and terminal metal–ligand distances experience a shortening of *ca*. 0.1 Å on reducing the co-ordination number of the metal centre from four to three.

The conformation of the aryl groups is strongly influenced by the steric hindrance exerted by the *ortho-tert*-butyl substituents, although there are no unusually close intramolecular contacts. The torsion angle between the Cd_2Se_2 ring and a plane through the terminal ligand, defined by Cd(1)-Se(2)-C(1), is 33.3°. The phenyl rings attached to the bridging seleniums are almost perpendicular to the Cd_2Se_2 plane, with a dihedral angle of 100.1°, and since selenium is pyramidal this allows one *orthotert*-butyl group of each bridging ligand to approach the cadmium atoms to give non-bonding distances of 3.36 [Cd(1*) \cdots C(34)] and 3.45 Å [Cd(1) \cdots C(35)]. By symmetry this occurs on both sides of the Cd₂Se₂ ring. Since the hydrogen atoms were not directly located, no reliable Cd \cdots H distances can be given.

Conclusion

With the sterically hindered 2,4,6-trisubstituted arenechalcogenolates $R_3C_6H_2E^-$ ($R = Me, Pr^i$ or Bu^i ; E = S or Se) a series of zinc and cadmium complexes can be prepared where the degree of association is controlled by the steric requirements of the ligands. As a consequence, complexes of unusually low metal co-ordination numbers may result, ranging from polymeric (R = Me) to oligomeric ($R = Pr^i$) and to dimeric ($R = Bu^i$). The latter complexes are volatile and sublime readily; they dissociate in non-co-ordinating solvents to give two-co-ordinate monomeric zinc and cadmium chalcogenolato complexes.

Experimental

Materials.—All experiments were carried out under argon using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium-benzophenone [diethyl ether, thf, light petroleum (b.p. 40–60 °C)], sodium (toluene) or calcium hydride (dichloromethane, acetonitrile). The NMR solvents were stored over 4Å molecular sieve under argon. The compounds 2,4,6-Me₃C₆H₂SH (R¹SH),¹⁴ 2,4,6-Prⁱ₃C₆H₂SH (R²SH),¹⁴ 2,4,6-Buⁱ₃C₆H₂SH (R³SH),¹⁵ 2,4,6-Buⁱ₃C₆H₂SeH,⁷ Zn[N(SiMe₃)₂]₂¹⁶ and Cd[N(SiMe₃)₂]₂¹⁶ were prepared as described. Infrared spectra were recorded on Mattson Polaris, Nicolet F20 and Perkin-Elmer 684 spectrometers, Raman spectra on a Bruker IFS 66 instrument equipped with a FRA 106 FT-Raman module, and NMR spectra on JEOL PMX-60 (¹H) and EX90Q (¹H, ¹³C, ⁷⁷Se) instruments.

Syntheses.—2,4,6-Me₃C₆H₂SeH.¹⁷ The compound 2,4,6-Me₃C₆H₂SeH (R¹SeH) was prepared from Li(C₆H₂Me₃-2,4,6) and powdered Se in Et₂O-thf, followed by acidification with 2 mol dm⁻³ HCl, b.p. 52–54 °C (0.08 mmHg). NMR (CDCl₃): ¹H, δ 1.40 (s, 1 H, SeH), 2.16 (s, 3 H, *p*-Me), 2.26 (s, 6 H, *o*-Me) and 6.76 (s, 2 H); ⁷⁷Se (CDCl₃) (0.5 mol dm⁻³ Ph₂Se₂ in CDCl₃ as external standard, referenced to neat Me₂Se), δ 24.77 [*J*(Se–H) 53.7 Hz].

(2,4,6-Pr¹₃C₆H₂Se)₂. To MgBrR² (70 mmol), prepared in quantitative yield from R²Br and I₂-activated Mg in refluxing thf, was added grey selenium (6.0 g, 76 mmol) at -60 °C. After warming to room temperature the mixture was treated with an excess of alkaline aqueous K₃[Fe(CN)₆]. The organic fraction was extracted with diethyl ether (2 × 150 cm⁻³) and dried over CaCl₂. The solvent was removed and the residue recrystallised from acetonitrile to give the product as bright orange crystals, m.p. 101–103 °C (10.08 g, 17.9 mmol, 51%) (Found: C, 63.9; H, 7.9. Calc. for C₃₀H₄₆Se₂: C, 63.8; H, 8.2%). NMR: ¹H (CCl₄), δ 0.99 (d, 12 H, J = 7 Hz), 1.18 (d, 6 H), 2.80 (spt, 1 H) and 3.57 (spt, 2 H); ⁷⁷Se [CDCl₃, relative to 60% (v/v) Me₂Se in CDCl₃], δ 569.

2,4,6-Prⁱ₃C₆H₂SeH (R²SeH). To R²₂Se₂ (1.0 g, 1.77 mmol) in thf (15 cm⁻³) at room temperature was added 1 mol dm⁻³ LiBHEt₃ in thf (3.55 cm⁻³, 3.55 mmol). The resulting pale yellow solution was cooled to -78 °C and treated with HBF₄·Et₂O (1.0 g, 6.18 mmol) via a syringe. The mixture was stirred at -78 °C for 10 min and then allowed to warm to room temperature. After replacing the solvent by light petroleum (b.p. 40–60 °C) and filtration, the product was isolated as an air-sensitive pale yellow oil (0.95 g, 3.4 mmol, 95%) which may be purified further by

^{*} By comparison, a rather longer Cd–Se_term bond length is found in the mononuclear anion $[Cd(SePh)_4]^{2-.13}$

| Atom | x | У | z | Atom | x | У | z |
|-------|-----------|-----------|-----------|-------|-----------|----------|----------|
| Cd(1) | 400.9(6) | 920.3(3) | 5234.3(3) | C(18) | 3154(11) | 3091(5) | 5932(5) |
| Se(1) | 203.4(7) | -180.9(3) | 5967.3(3) | C(19) | 800(7) | -55(3) | 6853(3) |
| Se(2) | 514.0(9) | 2115.1(4) | 5577.0(4) | C(20) | -45(7) | -14(3) | 7523(3) |
| C(1) | 1373(7) | 2409(3) | 4694(3) | C(21) | 1513(7) | 18(4) | 7632(4) |
| C(2) | 617(7) | 2492(3) | 4031(4) | C(22) | 1958(8) | 129(6) | 8440(4) |
| C(3) | -934(8) | 2610(4) | 3965(5) | C(23) | 2182(8) | -634(5) | 7414(4) |
| C(4) | -1303(10) | 3182(4) | 4467(6) | C(24) | 2073(8) | 604(4) | 7208(4) |
| C(5) | -1387(10) | 2833(6) | 3181(6) | C(25) | - 737(7) | 1(3) | 8168(3) |
| C(6) | -1781(8) | 1997(4) | 4126(6) | C(26) | -2119(7) | - 19(3) | 8179(3) |
| C(7) | 1296(7) | 2514(3) | 3387(4) | C(27) | - 2837(8) | 3(4) | 8904(4) |
| C(8) | 2656(7) | 2509(3) | 3375(3) | C(28) | -2104(14) | -407(11) | 9462(6) |
| C(9) | 3396(8) | 2531(4) | 2645(4) | C(29) | -2783(32) | 673(8) | 9195(11) |
| C(10) | 4581(16) | 2140(12) | 2681(8) | C(30) | -4191(15) | -219(14) | 8830(6) |
| C(11) | 3757(34) | 3178(7) | 2479(12) | C(31) | -2805(7) | -21(3) | 7504(3) |
| C(12) | 2581(16) | 2248(16) | 2031(7) | C(32) | -2213(6) | - 38(3) | 6833(3) |
| C(13) | 3378(8) | 2526(3) | 4044(4) | C(33) | -3156(7) | - 39(4) | 6134(3) |
| C(14) | 2779(7) | 2483(3) | 4709(3) | C(34) | -3118(10) | -713(4) | 5749(5) |
| C(15) | 3686(8) | 2560(4) | 5423(4) | C(35) | -2840(8) | 539(4) | 5614(4) |
| C(16) | 3894(12) | 1903(5) | 5843(5) | C(36) | -4611(8) | 69(5) | 6318(4) |
| C(17) | 5093(10) | 2805(7) | 5245(5) | | | | |

Table 5Fractional atomic coordinates ($\times 10^4$) for compound 12

 Table 6
 Analytical and physical data for zinc and cadmium chalcogenolato complexes

| | | Sublimation | | | Analysis (%) | | |
|-------------------|-----------|-------------|--------|-----------|--------------|-----------|--------------------------|
| Complex M.p. (°C) | M.p. (°C) | (°C) | Colour | Yield (%) | С | Н | S |
| 1 | > 295 | | White | 90 | 59.8 (61.1) | 6.0 (6.0) | 16.4 (15.3) |
| 2 | 275° | | White | 84 | 45.7 (46.8) | 4.5 (4.8) | . , |
| 3 | >295 | | White | 80 | 51.5 (52.1) | 5.3 (5.4) | 14.9 (15.5) |
| 4 | 400 | | White | 95 | 42.1 (42.5) | 4.4 (4.4) | () |
| 5 | d | | White | 50 | 58.3 (58.7) | 5.6 (5.6) | 10.9 (10.9) ^e |
| 6 | 300 | 200 | White | 87 | 61.7 (61.8) | 8.0 (7.9) | 10.9 (10.3) |
| 7 | > 250 ° | 230 | White | 72 | 52.9 (53.2) | 6.9 (6.9) | · · · · |
| 8 | | 170 | White | 83 | 69.4 (69.7) | 9.7 (9.4) | 10.2 (10.3) |
| 10 | 210° | | White | 60 | 60.5 (60.6) | 8.2 (8.2) | . , |
| 11 | d | | White | 75 | 61.0 (61.1) | 8.5 (8.5) | |
| 12 | 300 ° | 240 | Yellow | 78 | 56.9 (56.8) | 7.6 (7.7) | |

distillation at 60 °C (0.01 mmHg). NMR (C_6D_6): ¹H, δ 1.05 (s, 1 H, SeH), 1.33 (d, 18 H, *o*- and *p*-CHMe₂, J = 7), 2.87 (spt, 1 H), 3.65 (spt, 2 H) and 7.10 (s, 2 H); ⁷⁷Se, δ 9.78 [J(Se-H) 48.8 Hz].

Metal thiolato and selenolato complexes. The preparative method used is similar for all complexes and is exemplified below for $Zn(SR^3)_2$. The 2,4,6-trimethylbenzenechalcogenolato complexes of Zn and Cd are obtained as insoluble precipitates which are difficult to recrystallise; the sterically more hindered R^2 and R^3 complexes are soluble in hydrocarbons. Analytical data are given in Table 6.

 $Zn(SR^3)_2$ 8. To a solution of R³SH (1.0 g, 3.59 mmol) in light petroleum (10 cm⁻³) at room temperature was added Zn[N-(SiMe₃)₂]₂ (0.66 g, 1.71 mmol) *via* a syringe. A white precipitate was formed which was filtered off and recrystallised from toluene to give the product as colourless crystals (0.88 g, 1.42 mmol, 82.9%).

 $Cd(SR^{1})_{2}$ 3. Colourless microcrystals, 80%, m.p. > 295 °C. The compound has also been prepared from $Cd(NO_{3})_{2}$ -4H₂O, R¹SH and NEt₃ in methanol.

 $Cd(SR^{1})_{2}(py)_{2}$ 5. From $Cd(SR^{1})_{2}$ on recrystallisation from pyridine, as colourless crystals, 50%. The compound loses pyridine quantitatively on heating to 90 °C at 0.01 mmHg, and more slowly on standing.

Crystallographic Data Collection and Structure Determination.—Crystals of compound 12 suitable for X-ray diffraction were grown from toluene. X-Ray measurements were made on a crystal sealed under argon in a thin-walled glass capillary, using a CAD4 diffractometer and graphite-monochromated Mo-K α radiation [λ (Mo-K α) = 0.710 69 Å], operating in the ω -2 θ scan mode. After preliminary photographic examination, unitcell and intensity data were obtained following standard procedures.¹⁸

Crystal data. $C_{72}H_{116}Cd_2Se_4$, $M_r = 1522.38$, monoclinic prisms, space group $P2_1/n$, a = 10.038(2), b = 20.102(3), c = 18.245(2) Å, $\beta = 92.76(1)^\circ$, U = 3677.27 Å³, Z = 2, $D_c = 1.37$ g cm⁻³, F(000) = 1560, μ (Mo-K α) = 25.72 cm⁻¹.

Data collection. T = 294 K, $16 < \theta < 17^{\circ}$; sin $\theta/\lambda = 0.037$, 0.595; $0 \le h \le 11$, $0 \le k \le 23$, $-21 \le l \le 21$. Of the 7206 reflections measured, 6455 were unique ($R_{int} = 0.011$) and 3947 satisfied the condition $F_o > 3\sigma(F_o)$. An empirical absorption correction based on ψ scans was made, the maximum and minimum transmission being 1.0 and 0.95.

Structure solution and refinement. The structure was solved using the heavy-atom method and refined via full-matrix least squares. Non-hydrogen atoms were assigned anisotropic displacement factors; hydrogen atoms were inserted in idealised positions and refined in the riding mode with group isotropic displacement factors using the AFIX facility in SHELX 76.¹⁹ The total number of parameters refined was 428, and the final *R* and *R'* values were 0.046 and 0.057 respectively with weights $w = [\sigma^2(F_o) + 0.002F_o^2]^{-1}$. The maximum and minimum residuals in the final difference map were 0.55 and -0.43 e Å⁻³ respectively. All calculations were made on a T800 transputer hosted by an IBM/AT clone. Scattering factor data were from the usual tabulation.²⁰ Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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