Sterically Hindered Chalcogenolato Complexes. Mono- and Di-meric Thiolates and Selenolates of Zinc and Cadmium; Structure of [{Cd(SeC₆H₂But₃-2,4,6)₂}₂], the First Three-co-ordinate Cadmium–Selenium Complex†

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Protolysis of $M[N(SiMe_3)_2]_2$ (M = Zn or Cd) with arenechalcogenols $2,4,6-R_3C_6H_2EH$ (E = S or Se; R = Me, Pr^i or Bu^t) gives the corresponding chalcogenolato complexes $M(EC_6H_2R_3-2,4,6)_2$ in high yield. Complexes with R = Me form co-ordination polymers which are soluble only in strongly co-ordinating solvents. An adduct $[Cd(SC_6H_2Me_3-2,4,6)_2(py)_2]$ can be isolated which dissociates *in vacuo* with quantitative loss of pyridine (py). Complexes with R = Pr^i readily dissolve in poorly co-ordinating 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 $Zn(SeC_6H_2Bu^t_3-2,4,6)_2$ forms a 1:1 adduct with tetrahydrofuran. The structure of $[{Cd(SeC_6H_2Bu^t_3-2,4,6)_2}_2]$ 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 $[{Cd(SC_6H_4Me-p)_2}_n]$,[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 $[{M(ER)(\mu\text{-}ER)L}_2]$ (E = S or Se, L = N- or P-donor 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-*tert*-butylbenzenethiolato ligand produces an unusually low-co-ordinate 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 or Bu^t; E = S or Se).

Results and Discussion

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

$$MX_2 + 2REH + 2NEt_3 \longrightarrow M(ER)_2 + 2[NEt_3H]X \quad (1)$$
$$(R = \text{aryl})$$
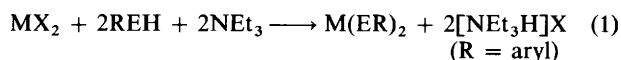
salt, the thiol and a tertiary amine as base in a polar solvent, we found this method less suitable for the preparation of complexes with ligands of high steric hindrance. Such complexes are best synthesised by the reaction of the metal bis(trimethylsilyl)amides with the thiol or selenol in a non-co-ordinating solvent, preferably in light petroleum [equation (2)].

M = Zn or Cd
E = S or Se
R = Me, Pr^i or Bu^t
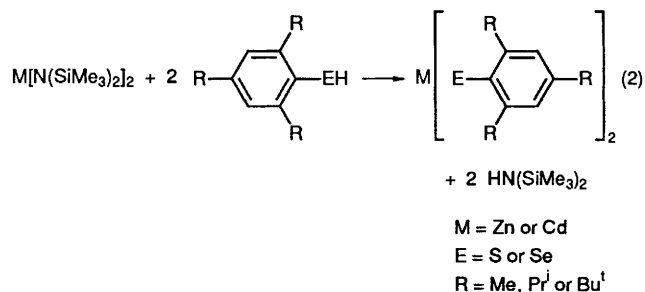
Neat 2,4,6-trimethylbenzeneselenol is prepared by the acidification of $LiSeC_6H_2Me_3-2,4,6$ obtained by treatment of mesityllithium with selenium powder, with aqueous HCl. Some dimesityl diselenide is formed as a by-product. A more generally applicable method for the synthesis of anhydrous selenols is the reduction of the diaryl diselenide with $LiBHEt_3$ in tetrahydrofuran (thf), followed by acidification with $HBF_4·Et_2O$ 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.

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† Bis[(μ-2,4,6-tri-*tert*-butylbenzeneselenolato-κ²*Se*)(2,4,6-tri-*tert*-butyl benzeneselenolato-κ*Se*)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 ≈ 133 Pa.

Table 1 Proton NMR data for zinc and cadmium chalcogenolates, $M(EC_6H_2R_3\text{-}2,4,6)_2$

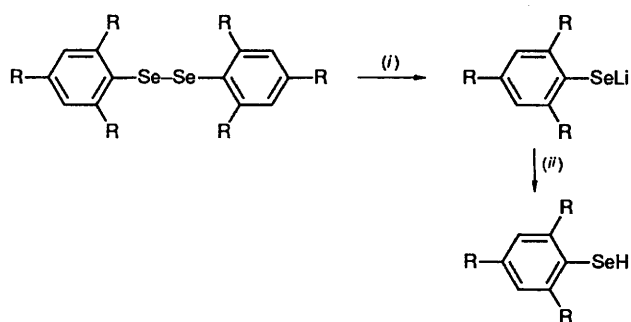| Complex	R	o-R	p-R	Aryl
1 Zn(SR¹)₂ [a]	Me	2.62 (s, 6 H)	2.18 (s, 3 H)	6.70 (s, 2 H)
2 Zn(SeR¹)₂ [a]	Me	2.68 (s, 6 H)	2.18 (s, 3 H)	6.77 (s, 2 H)
3 Cd(SR¹)₂ [a]	Me	2.63 (s, 6 H)	2.13 (s, 3 H)	6.72 (s, 2 H)
4 Cd(SeR¹)₂ [a]	Me	2.68 (s, 6 H)	2.18 (s, 3 H)	6.77 (s, 2 H)
6 Cd(SR²)₂ [b]	Prⁱ	0.81 (d, 12 H) 3.61 (spt, 2 H)	1.17 (d, 6 H, CHMe_2) 2.75 (spt, 1 H, CHMe₂, J = 7 Hz)	6.69 (s, 2 H)
7 Cd(SeR²)₂ [b]	Prⁱ	0.87 (d, 12 H) 3.59 (spt, 2 H)	1.11 (d, 6 H, CHMe_2) 2.73 (spt, 1 H, CHMe₂, J = 7 Hz)	6.77 (s, 2 H)
8 Zn(SR³)₂ [b]	Buᵗ	1.23 (s, 18 H)	1.04 (s, 9 H)	6.87 (s, 2 H)
9 [Zn(SR³)₂(OEt₂)] [b,c]	Buᵗ	1.60 (s, 18 H)	1.25 (s, 9 H)	7.40 (s, 2 H)
10 Zn(SeR³)₂ [b]	Buᵗ	1.40 (s, 18 H)	1.14 (s, 9 H)	7.20 (s, 2 H)
11 [Zn(SeR³)₂(thf)] [b,d]	Buᵗ	1.50 (s, 18 H)	1.20 (s, 9 H)	7.30 (s, 2 H)
12 Cd(SeR³)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, $M(EC_6H_2Bu^t_3\text{-}2,4,6)_2$ *

Zn(SR³)₂ 8	Zn(SeR³)₂ 10	[Zn(SeR³)₂(thf)] 11	Cd(SR³)₂	Cd(SeR³)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-CMe₃
31.6	31.5	31.5	31.5	31.6	para-CMe_3
		69.7			OCH₂ (thf)
		25.3			CH₂ (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, $M(EC_6H_2Me_3\text{-}2,4,6)_2$.—The mesityl chalcogenolato complexes Zn(SR¹)₂ **1**, Zn(SeR¹)₂ **2**, Cd(SR¹)₂ **3** and Cd(SeR¹)₂ **4** (R¹ = C₆H₂Me₃-2,4,6) 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-workers[1-3] 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(TeC₆H₂Me₃-

2,4,6)₂}∞],[8] it is probable that mesityl thiolates and selenolates of Zn and Cd also form polymeric chains rather than admantoid cages.

The compound Cd(SR¹)₂ forms a crystalline pyridine adduct, [Cd(SR¹)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(SeR¹)₂ is significantly more soluble than the SR¹ analogue, although none of these compounds exhibits appreciable volatility.

Tri(isopropyl)phenyl Complexes, $Me(EC_6H_2Pr^i\text{,}2,4,6)_2$.— The reaction of Cd[N(SiMe₃)₂]₂ with R²SH gives Cd(SR²)₂ **6** (R² = C₆H₂Prⁱ₃-2,4,6) 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, ligand-exchange processes become apparent, as indicated by a broadening of all proton signals and the loss of a coupling pattern for the CHMe₂ 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(SR²)₂ in a pure form; the

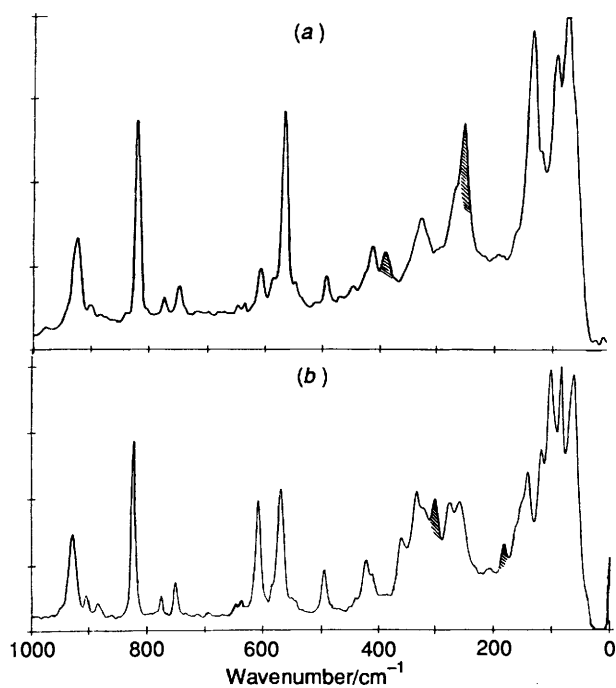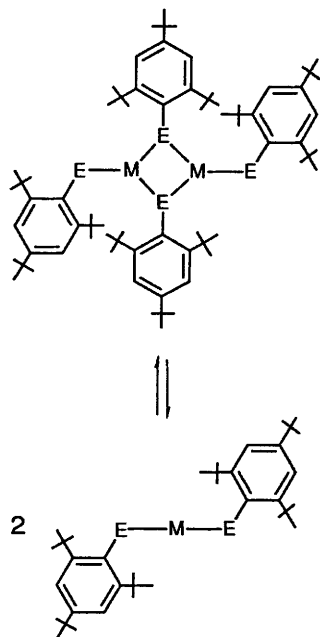**Fig. 1** Fourier-transform Raman spectra of thiolato complexes (*a*), $Zn(SR^3)_2$ and (*b*) $Cd(SR^3)_2$. Bands assigned to metal–sulphur vibrational modes are indicated by shading

Scheme 2

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*, $M(C_6H_2Bu^t_3-2,4,6)_2$.—The high steric hindrance provided by the 2,4,6-tri-*tert*-butylphenyl substituent (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 $CDCl_3$ is typical of a monomeric complex with a two-co-ordinate metal centre. The only change observed in cooling from 25 to $-50\,^\circ\text{C}$ is the
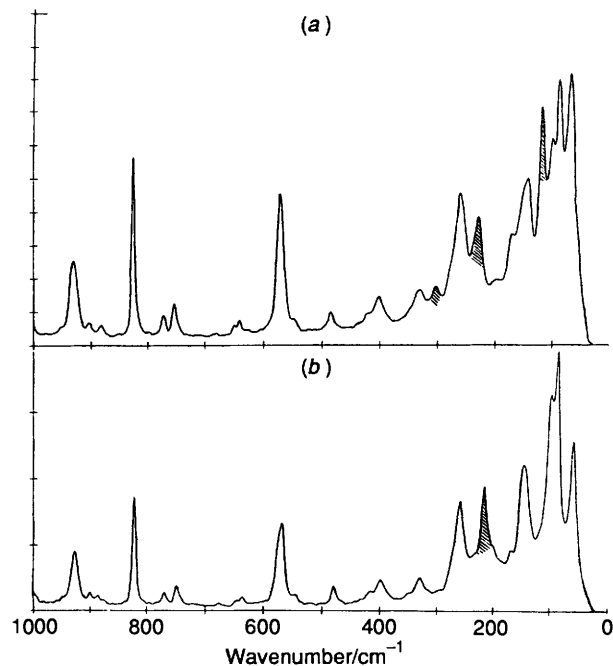

Fig. 2 Fourier-transform Raman spectra of selenolato complexes (*a*) $Zn(SeR^3)_2$ and (*b*) $Cd(SeR^3)_2$. Shading indicates bands due to metal–selenium vibrational modes

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 $Cd(SeR^3)_2$ 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 $Cd(SR^3)_2$, 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-co-ordinate linear structures are well documented for mercury,[11] $Cd(SR^3)_2$[7] and the zinc and cadmium tri-*tert*-butyl-benzenechalcogenolato 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 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.

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

$Zn(SR^1)_2$ 1	$Cd(SR^1)_2$ 3	$Zn(SR^1)_2$ 2	$Cd(SeR^1)_2$ 4	$Cd(SR^2)_2$ 6	$Cd(SeR^2)_2$ 7	$Zn(SR^3)_2$ 8	$Cd(SR^3)_2$[7]	$Zn(SeR^3)_2$ 10	$Cd(SeR^3)_2$ 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 v(M–E)			
				412m		(390s)			
				(407m)		v(M–E)			
405w	396wm					v(M–E)	(361s) v(M–E)		
(364m)							(339s) v(M–E)		
361w			349w			328m		331w	329w
325w	323w		325w				300m v(M–E)	303w v(M–E)	
(314m)	(322m)						(295s) v(M–E)	(296m) v(M–E)	
297w				(293m) v(M–E)			273m		
				285s (sh) v(M–E)					
							258m	260s	258m
(273s) v(M–E)				279s v(M–E)		255s v(M–E)			(257m) v(M–E)
								(230m) v(M–E)	(222s) v(M–E)
267w		(260w)	260m	(266s)				229m v(M–E)	215m v(M–E)
240w	(248s) v(M–E)				(205s) v(M–E)				
(226m) v(M–E)	(228m) v(M–E)					194w	181w v(M–E)	197vw	
	222w		217wm v(M–E)			139s v(M–E)	141m	143s	145s
	(210m) v(M–E)	(210s) v(M–E)	(203m)			120w (sh)	118w	118s v(M–E)	97m
			193m v(M–E)						
			(180s) v(M–E)	180m					
151s v(M–E)			159w	143m					
140s v(M–E)	130s v(M–E)								
121m			116vs v(M–E)	98vs					

* No Raman spectrum recorded due to fluorescence.

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.
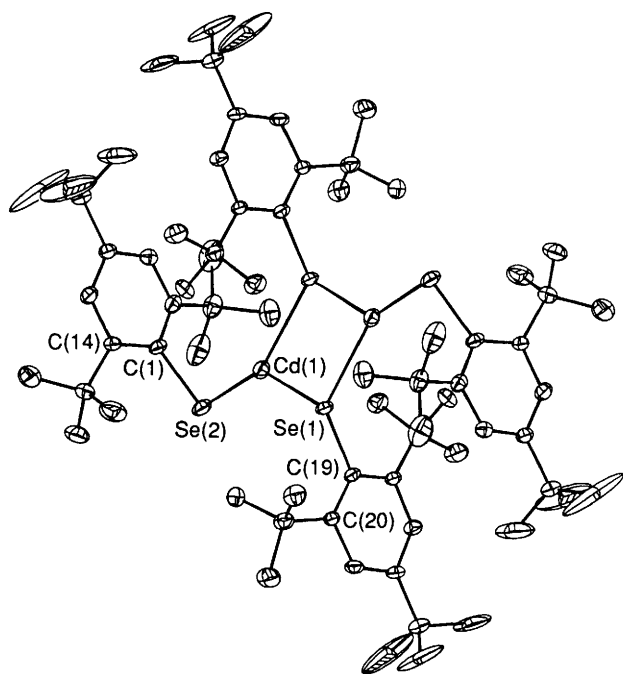
Fig. 3 Molecular structure of [{Cd(SeR³)₂}₂] **12**, showing the atomic numbering scheme

Table 4 Bond lengths (Å) and angles (°) for [{Cd(SeC₆H₂Buᵗ₃-2,4,6)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 [{Cd₂(μ-SePh)₂(SePh)₂L}∞] (L = Et₂PC₂H₄PEt₂) (2.678 and 2.564 Å)⁶ᵇ and in the cluster anion [cd₈(μ-S)(μ-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 Cd₂Se₂ ring and a plane through the terminal ligand, defined by Cd(1)–Se(2)–C(1), is 33.3°. The

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* By comparison, a rather longer Cd–Se_term bond length is found in the mononuclear anion [Cd(SePh)₄]²⁻.¹³

phenyl rings attached to the bridging seleniums are almost perpendicular to the Cd₂Se₂ plane, with a dihedral angle of 100.1°, and since selenium is pyramidal this allows one ortho-tert-butyl group of each bridging ligand to approach the cadmium atoms to give non-bonding distances of 3.36 [Cd(1*) ⋯ C(34)] and 3.45 Å [Cd(1) ⋯ C(35)]. By symmetry this occurs on both sides of the Cd₂Se₂ ring. Since the hydrogen atoms were not directly located, no reliable Cd ⋯ H distances can be given.

Conclusion

With the sterically hindered 2,4,6-trisubstituted arenechalcogenolates R₃C₆H₂E⁻ (R = Me, Prⁱ or Buᵗ; 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 = Prⁱ) and to dimeric (R = Buᵗ). 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-Buᵗ₃C₆H₂SH (R³SH),¹⁵ 2,4,6-Buᵗ₃C₆H₂SeH,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-Prⁱ₃C₆H₂Se)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

Table 5 Fractional atomic coordinates (× 10^4) for compound **12**

Atom	x	y	z	Atom	x	y	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 6 Analytical and physical data for zinc and cadmium chalcogenolato complexes

Complex	M.p. (°C)	Sublimation temperature[a] (°C)	Colour	Yield (%)	Analysis (%)[b] C	H	S
1	>295		White	90	59.8 (61.1)	6.0 (6.0)	16.4 (15.3)
2	275[c]		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[c]	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[c]		White	60	60.5 (60.6)	8.2 (8.2)	
11	d		White	75	61.0 (61.1)	8.5 (8.5)	
12	300[c]	240	Yellow	78	56.9 (56.8)	7.6 (7.7)	

[a] At 0.01 Torr (ca. 1.33 Pa). [b] Required values given in parentheses. [c] With decomposition. [d] Loss of donor ligand on heating. [e] N, 4.8 (4.9%).

distillation at 60 °C (0.01 mmHg). NMR (C$_6$D$_6$): ^{1}H, δ 1.05 (s, 1 H, SeH), 1.33 (d, 18 H, *o*- and *p*-CHMe_2, J = 7), 2.87 (spt, 1 H), 3.65 (spt, 2 H) and 7.10 (s, 2 H); ^{77}Se, 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 R^{3}SH (1.0 g, 3.59 mmol) in light petroleum (10 cm^{-3}) at room temperature was added Zn[N-(SiMe$_3$)$_2$]$_2$ (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$_3$)$_2$·4H$_2$O, R^{1}SH and NEt$_3$ 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-Kα radiation [λ(Mo-Kα) = 0.710 69 Å], operating in the ω–2θ scan mode. After preliminary photographic examination, unit-cell and intensity data were obtained following standard procedures.[18]

Crystal data. C$_{72}$H$_{116}$Cd$_2$Se$_4$, M_r = 1522.38, monoclinic prisms, space group $P2_1/n$, a = 10.038(2), b = 20.102(3), c = 18.245(2) Å, β = 92.76(1)°, U = 3677.27 Å^3, Z = 2, D_c = 1.37 g cm^{-3}, $F(000)$ = 1560, μ(Mo-Kα) = 25.72 cm^{-1}.

Data collection. T = 294 K, 16 < θ < 17°; sin θ/λ = 0.037, 0.595; 0 ≤ h ≤ 11, 0 ≤ k ≤ 23, −21 ≤ l ≤ 21. Of the 7206 reflections measured, 6455 were unique (R_{int} = 0.011) and 3947 satisfied the condition F_o > 3σ(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.

References
1 I. G. Dance, *J. Am. Chem. Soc.*, 1980, **102**, 3445.
2 D. Craig, I. G. Dance and R. G. Garbutt, *Angew. Chem.*, 1986, **98**, 178; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 165; I. G. Dance, R. G. Garbutt, D. C. Craig and M. L. Scudder, *Inorg. Chem.*, 1987, **26**, 4057; I. G. Dance, R. G. Garbutt, D. C. Craig, M. L. Scudder and T. D. Bailey, *J. Chem. Soc., Chem. Commun.*, 1987, 1164.
3 I. G. Dance, R. G. Garbutt and M. L. Scudder, *Inorg. Chem.*, 1990, **29**, 1571.
4 M. B. Hursthouse, O. Z. F. Khan, M. Mazid, M. Motevalli and P. O'Brien, *Polyhedron*, 1990, **9**, 541; E. Dubler and E. Gyr, *Inorg. Chem.*, 1988, **27**, 1466.
5 (a) D. T. Corwin, E. S. Gruff and S. A. Koch, *J. Chem. Soc., Chem. Commun.*, 1987, 966; (b) D. T. Corwin and S. A. Koch, *Inorg. Chem.*, 1988, **27**, 493; (c) S. J. Black, F. W. B. Einstein, P. C. Hayes, R. Kumar and D. G. Tuck, *Inorg. Chem.*, 1986, **25**, 4181.
6 (a) B. Kaptein, L. Wang-Griffin, G. Barf and R. M. Kellogg, *J. Chem. Soc., Chem. Commun.*, 1987, 1457; (b) J. G. Brennan, T. Siegrist, P. J. Carroll, S. M. Stuczynski, L. E. Brus and M. L. Steigerwald, *J. Am. Chem. Soc.*, 1989, **111**, 4141.
7 M. Bochmann, K. Webb, M. Harman and M. B. Hursthouse, *Angew. Chem.*, 1990, **102**, 703; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 638; M. Bochmann and K. Webb, *Abstr. 5th Int. Conf. Metalorganic Vapour Phase Epitaxy*, Aachen, 1990, p. 205.
8 M. Bochmann, A. P. Coleman, K. J. Webb, M. B. Hursthouse and M. Mazid, *Angew. Chem.*, in the press.
9 P. P. Power and S. C. Shoner, *Angew. Chem.*, 1990, **102**, 1484; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1403.
10 M. Bochmann and K. J. Webb, in *Chemical Perspectives of Microelectronic Materials II*, eds., L. V. Interrante, K. F. Jensen, L. H. Dubois and M. E. Gross, *Mater. Res. Soc. Symp. Proc.*, vol. 204, Material Research Society, New York, 1991, p. 149; K. J. Webb and J. E. Hails, unpublished work.
11 D. C. Bradley and N. R. Kunchur, *J. Chem. Phys.*, 1964, **40**, 2258; *Can. J. Chem.*, 1965, **43**, 2786; N. J. Taylor and A. J. Carty, *J. Am. Chem. Soc.*, 1977, **99**, 6143; C. Perchard, G. Zuppiroli, P. Gouzerh, Y. Jeannin and F. Roberts, *J. Mol. Struct.*, 1981, **72**, 119; H. Barrera, J. C. Bayon, P. Gonzales-Duarte, J. Sola, J. M. Vinas, J. L. Brianso, M. C. Brianso and X. Solans, *Polyhedron*, 1982, **1**, 647; W. Wojnowski, L. Wojnowski and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, 1985, **531**, 153; E. S. Gruff and S. A. Koch, *J. Am. Chem. Soc.*, 1990, **112**, 1245; E. Bock, M. Brito, M. Gernon, D. McGowty, H. Kang and J. Zubieta, *Inorg. Chem.*, 1990, **29**, 3172.
12 G. S. Lee, K. J. Fisher, D. C. Craig, M. L. Scudder and I. G. Dance, *J. Am. Chem. Soc.*, 1990, **112**, 6435.
13 N. Ueyama, T. Sugawara, K. Sasaki, A. Nakamura, S. Yamashita, Y. Wakatsuki, H. Yamazaki and N. Yasuoka, *Inorg. Chem.*, 1988, **27**, 741.
14 P. J. Blower, J. R. Dilworth, J. P. Hutchinson and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1985, 1533.
15 W. Rundel, *Chem. Ber.*, 1969, **102**, 358.
16 H. Bürger, W. Sawadny and U. Wannagat, *J. Organomet. Chem.*, 1965, **3**, 113.
17 G. Bwembya, M.Sc. Thesis, University of East Anglia, 1989.
18 R. A. Jones, M. B. Hursthouse, K. M. A. Malik and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
19 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
20 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.