Controlled Degradation of a Ligand-Deficient Complex: From [{$Cd(C_6F_5)(STrt)\}_4$] to [{$Cd(C_6F_5)(STrt)\}_3(OH)]^-$ and [$Cd(C_6F_5)(STrt)_2]^-$ (Trt = Triphenylmethyl)☆

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Bis(pentafluorophenyl)cadmium, [$Cd(C_6F_5)_2$], reacts with equimolar amounts of triphenylmethanethiol, TrtSH, in toluene to give [{$Cd(C_6F_5)(STrt)\}_4$] · 1.5 tol (**1**). The cuboidal complex of **1** has been transformed into the heterometallic cuboidal complex [{$Cd(C_6F_5)(STrt)\}_3(OH)K(THF)_3$] (**2**) by reaction with KOH in tetrahydrofuran. In the presence of 18-crown-6, the compound [K(18-crown-6)$(THF)_2$][{$Cd(C_6F_5)(STrt)\}_3(OH)$] · THF (**3**) has been obtained instead of **2**. X-ray structure analysis shows the anion of **3** to be an incomplete cuboidal complex, which alternatively can be described as a cyclic trimer of the {$Cd(C_6F_5)(STrt)$} unit stabilized by a μ_3-hydroxo ligand. The compound [K(18-crown-6)$(THF)_2$]-[$Cd(C_6F_5)(STrt)_2$] (**4**) has been isolated from reaction mixtures containing **1**, KSTrt and 18-crown-6. The cadmium atom in **4** is three-coordinated, in contrast to the cadmium atoms in **1**−**3**, which are situated in strongly distorted coordination tetrahedra. Intramolecular $C_6H_5\cdots C_6F_5\cdots C_6H_5$ stacks in **4** are interpreted as resulting from attractive ligand−ligand interactions. Spectroscopic data, particularly from ^{13}C-NMR and IR spectra, are consistent with the order of ligand deficiency: **1** > **2** > **3** > **4**. The macrocyclic, eight-coordinate complex [K(18-crown-6)$(THF)_2]^+$ in **3** and **4** contains *trans* arranged THF ligands.

Metal complexes having an overall donor-to-metal ratio which is smaller than the typical coordination number adopted with the respective donors can be termed “ligand-deficient“[1]. Ligand deficiency is accompanied by low coordination numbers and/or the formation of oligomeric species with bridging ligands, and − most important − by the tendency to bind additional ligands[2]. Of course, the simple arithmetic of this concept is only useful, if the reactivity is not determined by other factors such as metal−metal bonding or the character of the metal−ligand bonds.

We found that bis(pentafluorophenyl)cadmium, [$Cd(C_6F_5)_2$], is a suitable starting material for the synthesis of ligand-deficient chalcogenolato complexes of the general formula [$Cd_n(C_6F_5)_{2n-p}(ER)_p$] (E = O or S; R = alkyl, aryl)[1][3]. A convenient method for the preparation of [$Cd(C_6F_5)_2$] by thermal decarboxylation of $Cd(O_2CC_6F_5)_2$ has been described by Schmeißer and Weidenbruch[4]. Crystals of [$Cd(C_6F_5)_2$] consist of two-coordinate monomers, as shown by X-ray structure determination[5]. Protolysis reactions with alcohols and thiols according to Eq. 1 allowed the syntheses of several new multinuclear complexes, most of which were also characterized by X-ray crystal structure analysis[1][3][6].

$$n\,[Cd(C_6F_5)_2] + p\ REH \rightarrow [Cd_n(C_6F_5)_{2n-p}(ER)_p] + p\ C_6F_5H \qquad (1)$$

One of these complexes is [{$Cd(C_6F_5)(STrt)\}_4$] [Trt = triphenylmethyl (“trityl“)], whose preparation and typical ligand-deficient behaviour towards the nucleophiles HO^- and $TrtS^-$ are described in this paper. The crystal structures of the resulting degradation products, a tri- and a mononuclear complex, respectively, are presented.

Syntheses

Starting from [$Cd(C_6F_5)_2$], we have studied various reactions, which are shown in Schemes 1 and 2. The partial protolysis of [$Cd(C_6F_5)_2$] with triphenylmethanethiol (TrtSH) in toluene (Eq. 2) yields [{$Cd(C_6F_5)(STrt)\}_4$] · 1.5 tol (**1**). X-ray structure analysis has revealed that **1** contains a cuboidal $\{Cd_4(\mu_3\text{-}SR)_4\}^{4+}$ core, which is structurally very similar to that of the already described *t*BuS$^-$ analogue[1]. The X-ray structure of **1** is therefore not included here, but will be detailed in a forthcoming paper together with the structure of the *di*nuclear alkoxo complex [{$Cd(C_6F_5)(OTrt)\}_2$][6].

1 exhibits the characteristic reactivity of a ligand-deficient complex towards potential ligands. It is degraded to the trinuclear complex [{$Cd(C_6F_5)(STrt)\}_3(OH)]^-$ by reaction with the appropriate amount of hydroxide (Eqs. 3 and 4). The potassium hydroxide used in this reaction must be prepared in situ from potassium metal and water to be sufficiently reactive. Depending on whether or not 18-crown-6 has been added, [K(18-crown-6)$(THF)_2$][{$Cd(C_6F_5)(STrt)\}_3$-(OH)] · THF (**3**) or [{$Cd(C_6F_5)(STrt)\}_3(OH)K(THF)_3$] (**2**), respectively, can be isolated. The anion of **3** is an incomplete cuboidal complex (see Scheme 2), whose structure will be discussed below. The structure of **2** has been unambiguously established from single-crystal X-ray diffraction data.

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Scheme 1

$$4\,[Cd(C_6F_5)_2] + 4\,TrtSH \xrightarrow[-4\,C_6HF_5]{toluene} \underset{\mathbf{1}}{[\{Cd(C_6F_5)(STrt)\}_4]\cdot 1.5\,tol} \qquad (2)$$

$$3\,[\{Cd(C_6F_5)(STrt)\}_4] + 4\,KOH \xrightarrow{THF} 4\,\underset{\mathbf{2}}{[\{Cd(C_6F_5)(STrt)\}_3(OH)K(THF)_3]} \qquad (3)$$

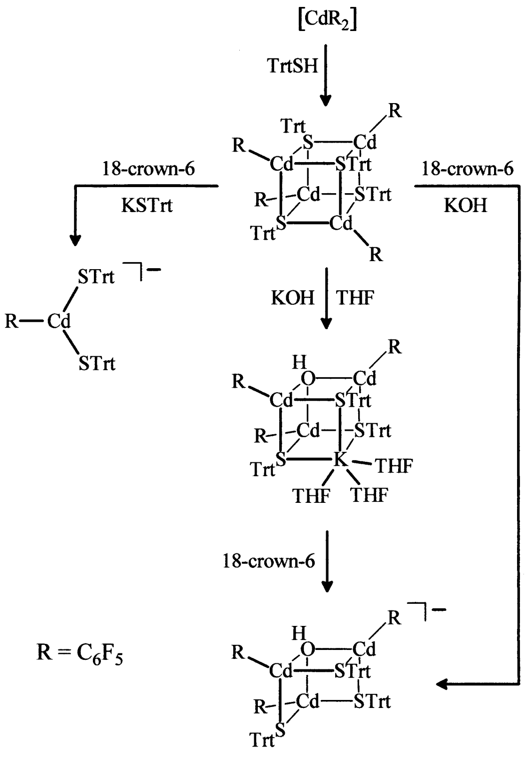
$$3\,[\{Cd(C_6F_5)(STrt)\}_4] + 4\,KOH + 4\ 18\text{-crown-6} \xrightarrow{THF} 4\,\underset{\mathbf{3}}{[K(18\text{-crown-6})(THF)_2][\{Cd(C_6F_5)(STrt)\}_3(OH)]\cdot THF} \qquad (4)$$

$$[\{Cd(C_6F_5)(STrt)\}_3(OH)K(THF)_3] + 18\text{-crown-6} \xrightarrow{THF} \underset{\mathbf{3}}{[K(18\text{-crown-6})(THF)_2][\{Cd(C_6F_5)(STrt)\}_3(OH)]\cdot THF} \qquad (5)$$

$$0.5\,[\{Cd(C_6F_5)(STrt)\}_4] + KSH + 18\text{-crown-6} \xrightarrow[-C_6HF_5]{THF} \underset{\mathbf{4}}{[K(18\text{-crown-6})(THF)_2][Cd(C_6F_5)(STrt)_2]} + CdS\downarrow \qquad (6)$$

$$[\{Cd(C_6F_5)(STrt)\}_4] + 4\,KSTrt + 4\ 18\text{-crown-6} \xrightarrow[toluene]{THF/} 4\,\underset{\mathbf{4}}{[K(18\text{-crown-6})(THF)_2][Cd(C_6F_5)(STrt)_2]} \qquad (7)$$

Scheme 2



Unfortunately, the crystal quality was low, and thus the structure determination does not meet the usual standards. Therefore, only some basic crystal data are given here (see Experimental Section). **2** can be transformed into **3**: the $\{K(THF)_3\}^+$ group is removed by addition of 18-crown-6 (Eq. 5).

Interestingly, the reaction of **1** with monohydrogensulphide differs strongly from that with hydroxide. The SH^- ends up completely as cadmium sulphide (Eq. 6). We have already noticed the same type of different behaviour between H_2S and H_2O when reacted with $[Cd(C_6F_5)_2]$. With H_2S the only isolable product is CdS[1], while the partial hydrolysis of $[Cd(C_6F_5)_2]$ yields $[\{Cd(C_6F_5)(OH)\}_4]$, which could be isolated and structurally characterized by Weidenbruch et al.[7]. The second product in Eq. 6, namely the new compound $[K(18\text{-crown-6})(THF)_2][Cd(C_6F_5)(STrt)_2]$ (**4**), is more conveniently prepared from **1**, KSTrt and 18-crown-6 according to Eq. 7. The compounds **1**−**4** decompose on exposure to air, **4** apparently being most sensitive.

It is worth noting, that triphenylmethanethiolate has rarely been used as a sterically hindered ligand[8], especially when the wealth of data on bulky *aromatic* thiolate ligands is considered[9]. The main reason for this seems to be the fear, that C−S bond cleavage may occur. The C−S bonds of aliphatic thiols are in fact weaker than those of aromatic thiols. In some cases, C−S scission reactions have even led to isolable sulfido complexes[10]. However, in the syntheses of the compounds **1**−**4** the use of triphenylmethanethiol(ate) has been found unproblematic[11].

Spectroscopic Properties

The ^{13}C-NMR spectra reflect the decrease of ligand deficiency, i. e. the decreasing electronic stress of the thiolate ligands, in the sequence **1**→**2**→**3**→**4**. The signal of the α-C atoms of the $TrtS^-$ groups is found at $\delta = 74.20$ (**1**), 65.78 (**2**), 63.81 (**3**), and 63.30 (**4**), respectively. The chemical-shift difference between **2** and **3** may indicate, that for **2** the coordination of $\{K(THF)_3\}^+$ by the $[\{Cd(C_6F_5)(STrt)\}_3(OH)]^-$ anion, as found in the solid state, is retained in solution. However, the influence of the different solvents is difficult to estimate (**2**: C_6D_6, **3**: $CDCl_3$). A clear, but reverse trend is also observed for the *ipso*-C atoms of the $TrtS^-$ ligands: $\delta = 147.0$ (**1**), 149.8 (**2**), 150.1 (**3**), and 153.6 (**4**), respectively. The remaining ^{13}C-NMR signals of the phenyl groups were found to be relatively insensitive to the coordination mode of the TrtS$^-$ ligand (μ_3, μ_2 or terminal). They span ranges of less than 2.0 ppm each.

The C_6F_5 ligands are terminally coordinated in all four compounds. Here, some less pronounced trends of the spectroscopic properties are observed: (i) for the ^{19}F-NMR signal of the *para*-F atom: $\delta = -156.7$ (**1**), -158.0 (**2**), and -160.4 (**3** and **4**), respectively, and (ii) for the C−F stretching frequency in the IR spectra: 954 (**1**), 949 (**2**), 948 (**3**), and 945 cm^{-1} (**4**), respectively. For the educt $[Cd(C_6F_5)_2]$ the C−F stretching vibration has been observed at 956 cm^{-1} [4]. A dependence of ν(C−F) on the metal oxidation state has been reported for pentafluorophenyl complexes of palladium and platinum: M^{IV} 968 ± 3, M^{II} 955 ± 6, and M^{I} 946 ± 6 cm^{-1} [12]. Thus, an increase in ligand deficiency shifts ν(C−F) into the same direction as an increasing oxidation state of the coordination centre does − in accordance with chemical intuition.

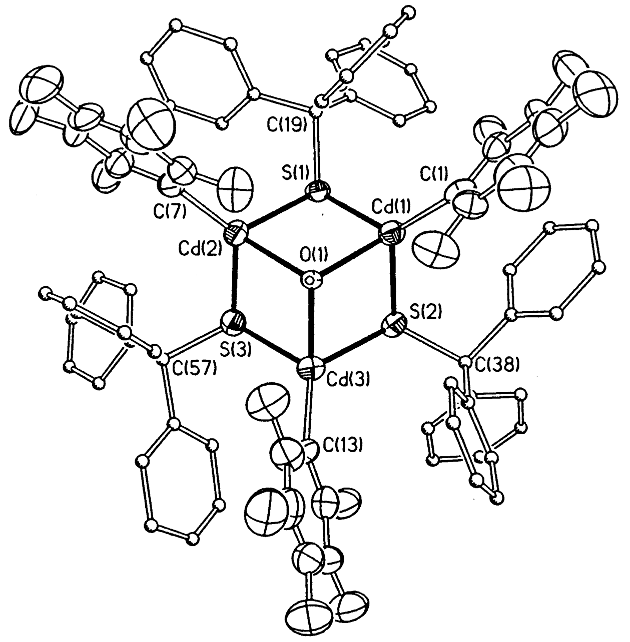
In the TrtS$^-$ ligands of **4** two types of *ortho*-H atoms can be distinguished by ^{1}H-NMR spectroscopy. Their intensity ratio of 2:1 is consistent with a structure that possesses an intramolecular $C_6H_5\cdots C_6F_5\cdots C_6H_5$ stack as observed in the solid state and discussed below.

X-ray Crystal Structures of 3 and 4

Crystals of **3** consist of $[\{Cd(C_6F_5)(STrt)\}_3(OH)]^-$ complexes, $[K(18\text{-crown-}6)(THF)_2]^+$ counterions and non-coordinating THF molecules. The trinuclear cadmium complex is shown in Figure 1. It can be regarded as a cyclic trimer of the $\{Cd(C_6F_5)(STrt)\}$ unit stabilized by a μ_3-hydroxo ligand. An alternative description is that of an incomplete cuboidal complex. As shown in Scheme 2, this complex can actually be prepared by removal of the $\{K(THF)_3\}^+$ corner from the heterometallic cuboidal complex $[\{Cd(C_6F_5)(STrt)\}_3(OH)K(THF)_3]$ (**2**). A structurally related, but homoleptic trinuclear complex has been described, namely $[Cd_3\{SC_6H_2(i\text{Pr})_3\text{-}2,4,6\}_7]^-$ [13].

The $[\{Cd(C_6F_5)(STrt)\}_3(OH)]^-$ complex in **3** closely approaches C_3 symmetry. Its central, chair-like Cd_3S_3 ring is strongly puckered, the metal part being contracted by the small μ_3-OH$^-$ ligand. This contraction becomes obvious by comparison with the situation in $[\{Cd(C_6F_5)(STrt)\}_4]$[6]: for **3** a shortening of the mean Cd···Cd distance (**3**: 3.57 Å) by 0.36 Å, an increase of the mean S−Cd−S angle by 9°, and a decrease of the mean Cd−S−Cd angle by 7° are observed. The coordination tetrahedra around the cadmium atoms are severely distorted with bond angles ranging from 87.6° for S−Cd−O to 130.4° for S−Cd−C (mean values). As may be expected from the different coordination modes of the thiolate, in **3** the mean Cd−S bond length (2.56 Å) is smaller than in **1** (2.65 Å), but larger than in **4** (2.467(1) Å) and in $[Cd(STrt)_2(tmeda)]$ (2.44 Å)[8b], where the ligands are terminally bonded.

Figure 1. View of the complex $[\{Cd(C_6F_5)(STrt)\}_3(OH)]^-$ in crystals of **3**; the hydrogen atoms of the thiolate ligands have been omitted for clarity; thermal ellipsoids are drawn with 30% probability[a]

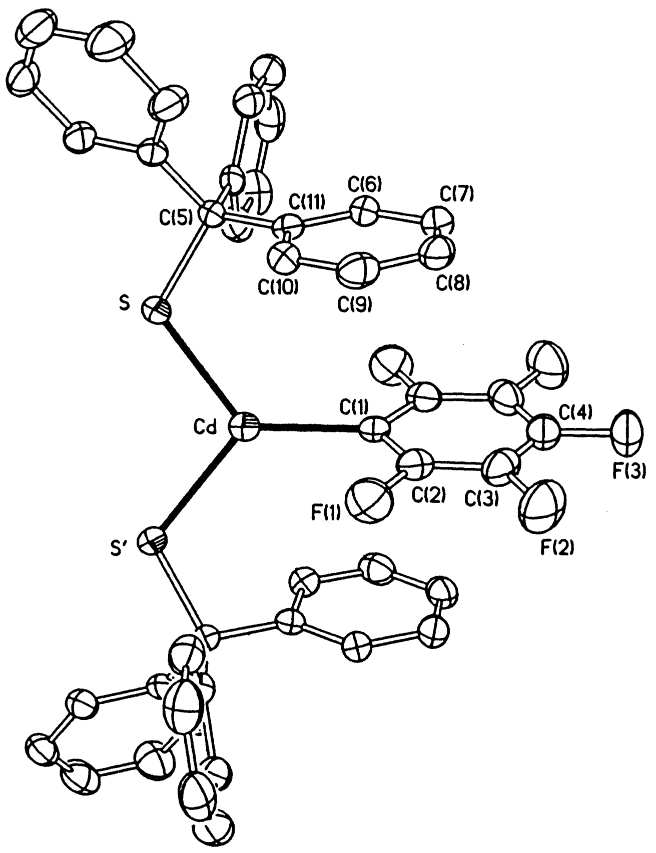


[a] Selected bond lengths [Å] and angles [°], mean values in brackets: Cd(1)−S(1) 2.542(3), Cd(1)−S(2) 2.586(3), Cd(2)−S(1) 2.568(3), Cd(2)−S(3) 2.545(3), Cd(3)−S(2) 2.563(3), Cd(3)−S(3) 2.583(3), Cd(1)−O(1) 2.395(6), Cd(2)−O(1) 2.408(7), Cd(3)−O(1) 2.368(7), Cd(1)−C(1) 2.16(1), Cd(2)−C(7) 2.18(1), Cd(3)−C(13) 2.20(1), S(1)−C(19) 1.87(1), S(2)−C(38) 1.89(1), S(3)−C(57) 1.87(1), S−Cd−S 90.91(9)−95.16(9) [93.0], S−Cd−O 86.0(2)−88.5(2) [87.6], S−Cd−C 126.1(3)−135.4(3) [130.4], O−Cd−C 111.4(4)−114.3(4) [113.1], Cd−S−Cd 87.4(1)−88.76(9) [88.2], Cd−O−Cd 95.7(3)−98.2(3) [96.6].

Crystals of **4** are composed of $[Cd(C_6F_5)(STrt)_2]^-$ anions and $[K(18\text{-crown-}6)(THF)_2]^+$ cations. The cadmium complex (see Figure 2) is situated on a crystallographic twofold axis of rotation, which passes through the atoms Cd, C(1), C(4), and F(3). To our knowledge, $[Cd(C_6F_5)(STrt)_2]^-$ is the first cadmium complex reported to have an S_2C donor set[14][15]. The observed bond lengths and angles at the Cd atom are unexceptional. There is, however, a striking structural features of this complex, namely the mutual orientation of the trityl groups and the pentafluorophenyl ligand. The C_6H_5 ring containing the C atoms C(6) to C(11) and the symmetry related one in the same complex are arranged above and below the C_6F_5 group. A $C_6H_5\cdots C_6F_5\cdots C_6H_5$ intramolecular stack results, in which the plane of the C_6F_5 group forms an angle of 4.6° with each of the C_6H_5 planes. The atom C(1) lies nearly perpendicular over the centroid of the C_6 ring of the phenyl group (deviation: ca. 1.0°). The C(1)···centroid distance is 3.37 Å.

The alternating stacking in complexes between polyfluorinated and non-fluorinated aromatic molecules is a well-known structural phenomenon in organic chemistry. Dahl has studied a number of such molecular complexes containing hexafluorobenzene as the fluorinated component[16]. He has reported mean interplanar distances in the stacks ranging from 3.39 to 3.56 Å. These values correspond approximately to the van der Waals thickness of typical aromatic molecules of 3.4 Å[17]. When viewed perpendicular to the ring planes, a slipped orientation of adjacent rings is usually observed. This is also true for the $C_6H_5\cdots C_6F_5$ pairs in **4**. The close structural similarity to the molecular complex *p*-xylene−hexafluorobenzene[18] is shown in Figure 3. Recent

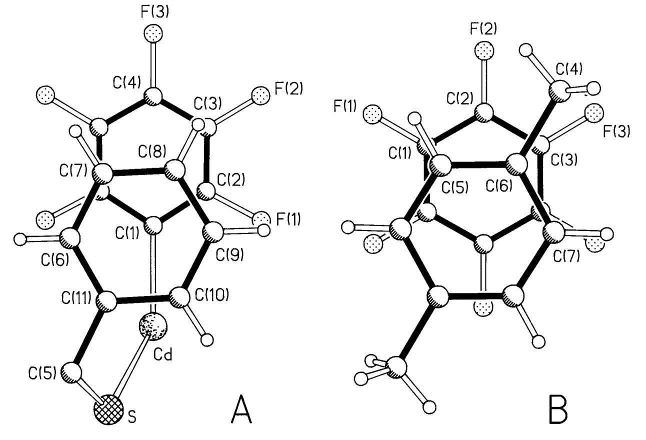
Figure 2. View of the complex $[Cd(C_6F_5)(STrt)_2]^-$ in crystals of **4**; hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn with 30% probability[a]



[a] Selected bond lengths [Å] and angles [°]: Cd−S 2.467(1), Cd−C(1) 2.180(6), S−C(5) 1.876(4), S−Cd−S' 103.39(5), S−Cd−C(1) 128.31(3), Cd−S−C(5) 111.7(1).

results indicate, that the attractive forces between polyfluorinated and non-fluorinated aromatic molecules are largely electrostatic in nature[19].

Figure 3. The slipped parallel arrangement of aromatic rings in $[Cd(C_6F_5)(STrt)_2]^-$ (A) and in the *p*-xylene−hexafluorobenzene molecular complex[18] (B); the mean C_6 planes of the fluorine-containing groups are exactly parallel to the projection plane; small circles represent hydrogen atoms.



We believe, that attractive interligand interactions are the most probable cause of the $C_6H_5\cdots C_6F_5\cdots C_6H_5$ stacking in **4**. No other *intra*molecular causes can be recognized. In fact, the sterical demand of the thiolate ligands should favour other arrangements, especially those with one trityl group above and the other below the $CdS_2C(1)$ plane. The possibility cannot be ruled out, however, that packing forces contribute to determine the observed structure. Regarding the expected weakness of $C_6H_5\cdots C_6F_5$ interactions[19b][20], the ^{1}H-NMR results on **4** (see above) should not be interpreted as a proof, but merely as a possible indication of aromatic-ring stacking in solution. Intramolecular stacks of phenyl and pentafluorophenyl groups are also observed in crystals of the compounds **1**−**3** (cf. Figure 1). In these cases, it cannot be decided whether or not these arrangements are enforced by sterical crowding. The face-to-face orientation of C_6H_5 and C_6F_5 groups in metal complexes is not particularly rare, though it has mostly been neglected in structure discussions. The Cambridge Structural Database (CSD)[14] contains ca. 30 examples where in metal coordination spheres attractive interactions of the type described above seem possible. A detailed analysis is, however, beyond the scope of this paper.

In both **3** and **4**, the cationic part is formed by the macrocyclic complex $[K(18\text{-crown-}6)(THF)_2]^+$. The CSD[14] lists four other structures containing this complex[21]. The metal ion in $[K(18\text{-crown-}6)(THF)_2]^+$ is in an O_8 environment, the THF ligands being in *trans* position. The mean K−O(macrocycle) bond lengths are 2.79 (**3**) and 2.80 Å (**4**), respectively. Due to disorder of the THF ligands in both compounds, the K−O(THF) bond lengths are less accurate. Their mean values are 2.78 (**3**) and 2.76 Å (**4**), respectively.

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Experimental Section

General: Bis(pentafluorophenyl)cadmium was prepared from $Cd(O_2CC_6F_5)_2$ according to a literature method[4]. Triphenylmethanethiol (Merck) was treated with activated charcoal in boiling ethanol and recrystallized twice from diethyl ether prior to use. Tetrahydrofuran was pretreated with KOH and subsequently destilled from $LiAlH_4$ under nitrogen. Toluene and *n*-hexane were refluxed over Na/K alloy and destilled under nitrogen. All other commercially available chemicals were used as received. The cadmium complexes described below were prepared and handled under an atmosphere of dry nitrogen in a glove box; storage was also under dry nitrogen. − IR: Bio-Rad FTS 7PC and Beckman IR-4220. − ^{1}H and $^{13}C\{^1H\}$ NMR: Bruker AM-300, chemical shifts relative to TMS, solvent signal as internal reference in the ^{13}C-NMR spectra ($CDCl_3$: $\delta_c = 77.00$, C_6D_6: $\delta_c = 128.00$). ^{19}F NMR: chemical shifts relative to $CFCl_3$. Prior to use, all NMR solvents were treated with molecular sieves to remove water. − Elemental analyses: Mikroanalytisches Laboratorium Beller, D-37004 Göttingen, Germany. − *Caution!* Cadmium compounds are highly toxic and probably carcinogenic. Therefore they should be handled with care to avoid exposure.

$[\{Cd(C_6F_5)(STrt)\}_4]\cdot 1.5$ tol (**1**): 2.76 g (10.0 mmol) of triphenylmethanethiol, dissolved in 10 ml of toluene, was added to a solution of 4.47 g (10.0 mmol) of $[Cd(C_6F_5)_2]$ in 25 ml of toluene.

After some minutes, a white, microcrystalline precipitate of **1** started separating from the yellow solution. The product was isolated within the next hour (on prolonged standing, a brown colouring occurred), thoroughly washed with toluene and dried in vacuo. Yield: 5.42 g (92%), m.p. 145°C (dec.). − IR (KBr): $\tilde{\nu}$ = 954 cm^{-1} (s, CF). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.44 (tol), 74.20 (Ph_3*C*), 125.3 (tol), 127.2 (Ph-*para* in Ph_3C), 127.9 (Ph-*meta* in Ph_3C), 128.2 (tol), 129.0 (tol), 129.7 (Ph-*ortho* in Ph_3C), 137.9 (tol), 147.0 (Ph-*ipso* in Ph_3C)[22]. − ^{19}F NMR (188.3 MHz, $CDCl_3$): δ = −109.3 (m, 8 F, C_6F_5-*ortho*), −156.7 (m, 4 F, C_6F_5-*para*), −162.0 (m, 8 F, C_6F_5-*meta*). − $C_{110.5}H_{72}Cd_4F_{20}S_4$ (2357.7): calcd. C 56.29, H 3.08, Cd 19.07, F 16.12, S 5.44; found C 55.81, H 3.02, Cd 19.14, F 16.2, S 5.63.

[{Cd(C$_6$F$_5$)(STrt)}$_3$(OH)K(THF)$_3$] (**2**): 39 mg (1.0 mmol) of freshly cut potassium metal was added to a solution of 18 μl (1.0 mmol) of water in 8 ml of tetrahydrofuran. After stirring overnight, a suspension of potassium hydroxide had formed. Traces of unreacted potassium were removed. 1.77 g (0.75 mmol) of **1**, dissolved in 12 ml of tetrahydrofuran, was added. The reaction mixture was stirred until the potassium hydroxide had completely reacted. Then the clear, colourless solution was carefully layered with *n*-hexane in the reaction flask. After 2 d, colourless crystals of **2** had separated, which were isolated on a large-pored glass filter, washed with *n*-hexane and dried in vacuo. Yield 1.20 g (62%), m.p. 146−147°C. − IR (KBr): $\tilde{\nu}$ = 949 cm^{-1} (s, CF). − ^1H NMR (300 MHz, CD_3CN): δ = 1.80 (m, 12 H, CCH_2C), 2.11 (br., 1 H, OH), 3.65 (m, 12 H, CH_2O), 6.91−7.03 (m, 27 H, Ph-*meta* and -*para*), 7.14 ("d", 18 H, Ph-*ortho*). − ^{13}C NMR (75.5 MHz, C_6D_6): δ = 25.68 (C*C*H_2C), 65.78 (Ph_3*C*), 67.77 (CH_2O), 126.8 (Ph-*para*), 127.7 (Ph-*meta*), 129.9 (Ph-*ortho*), 149.8 (Ph-*ipso*)[22]. − ^{19}F NMR (188.3 MHz, C_6D_6): δ = −110.8 (m, 6 F, C_6F_5-*ortho*), −158.0 (m, 3 F, C_6F_5-*para*), −161.9 (m, 6 F, C_6F_5-*meta*). − Crystallographic data (23°C): monoclinic, space group $P2_1/n$, a = 15.07(1), b = 21.75(1), c = 25.49(1) Å, β = 90.89(5)°, V = 8354 Å^3, Z = 4, $\rho_{calcd.}$ = 1.540 gcm^{-3}. − $C_{87}H_{70}Cd_3F_{15}KO_4S_3$ (1937.0): calcd. C 53.95, H 3.64, Cd 17.41, F 14.71, K 2.02, S 4.97; found C 53.07, H 3.70, Cd 17.57, F 14.1, K 2.10, S 4.62.

[K(18-crown-6)(THF)$_2$][{Cd(C$_6$F$_5$)(STrt)}$_3$(OH)]·THF (**3**): *Method A*: In tetrahydrofuran, potassium hydroxide was prepared as described above for **2**, but with the addition of 264 mg (1.00 mmol) of 18-crown-6. To the suspension 1.77 g (0.75 mmol) of **1**, dissolved in 12 ml of tetrahydrofuran, was added. After the reaction mixture had become clear, it was diluted with 15 ml of toluene and then layered with *n*-hexane. **3** separated as a colourless, crystalline solid, which was isolated, washed with *n*-hexane and dried in vacuo. Yield 1.49 g (68%), m.p. 165−166°C. − IR (KBr): $\tilde{\nu}$ = 948 cm^{-1} (s, CF). − ^1H NMR (300 MHz, CD_3CN): δ = 1.80 (m, 12 H, CCH_2C), 2.12 (br., 1 H, OH), 3.56 (s, 24 H, 18-crown-6), 3.64 (m, 12 H, CH_2O in THF), 7.02−7.13 (m, 27 H, Ph-*meta* and -*para*), 7.32 ("d", 18 H, Ph-*ortho*). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.58 (C*C*H_2C), 63.81 (Ph_3*C*), 67.93 (CH_2O in THF), 70.18 (18-crown-6), 125.6 (Ph-*para*), 126.8 (Ph-*meta*), 129.7 (Ph-*ortho*), 150.1 (Ph-*ipso*)[22]. − ^{19}F NMR (188.3 MHz, $CDCl_3$): δ = −110.9 (m, 6 F, C_6F_5-*ortho*), −160.4 (m, 3 F, C_6F_5-*para*), −163.7 (m, 6 F, C_6F_5-*meta*). − $C_{99}H_{94}Cd_3F_{15}KO_{10}S_3$ (2201.3): calcd. C 54.02, H 4.30, Cd 15.32, F 12.95, K 1.78, S 4.37; found C 53.98, H 4.35, Cd 15.14, F 13.0, K 1.92, S 4.50.

Method B: 0.97 g (0.50 mmol) of **2** was dissolved in 20 ml of tetrahydrofuran. To the stirred solution 132 mg (0.50 mmol) of 18-crown-6 was added. After the crown ether had dissolved, first toluene and then *n*-hexane were carefully layered over the reaction mixture. Nearly colourless crystals of **3** separated during the next 4 d. The product was isolated, washed with *n*-hexane and dried in vacuo. Yield 0.94 g (85%).

[K(18-crown-6)(THF)$_2$][Cd(C$_6$F$_5$)(STrt)$_2$] (**4**): 39 mg (1.0 mmol) of freshly cut potassium metal was added to a stirred solution of 276 mg (1.00 mmol) of triphenylmethanethiol in 2 ml of tetrahydrofuran. After ca. 4 h, the metal had completely reacted, and a clear, light yellow solution had formed. This solution was slowly dropped into a solution of 589 mg (0.250 mmol) of **1** in 2 ml of toluene. 264 mg (1.00 mmol) of 18-crown-6 was added. Then *n*-hexane was carefully layered over the light brown solution in the reaction flask. After 2 d, nearly colourless crystals of **4** had formed, which were isolated on a large-pored glass filter, washed with *n*-hexane, dried in vacuo, and finally stored in a refrigerator. Yield 1.01 g (79%). − IR (KBr): $\tilde{\nu}$ = 945 cm^{-1} (s, CF). − ^1H NMR (300 MHz, CD_3CN): δ = 1.80 (m, 8 H, CCH_2C), 3.56 (s, 24 H, 18-crown-6), 3.64 (m, 8 H, CH_2O in THF), 7.00−7.14 (m, 18 H, Ph-*meta* and -*para*), 7.33 ("d", 8 H, Ph-*ortho*), 7.47 ("d", 4 H, Ph-*ortho*). − ^{13}C NMR (75.5 MHz, C_6D_6): δ = 25.78 (C*C*H_2C), 63.30 (Ph_3*C*), 67.77 (CH_2O in THF), 70.16 (18-crown-6), 125.3 (Ph-*para*), 127.3 (Ph-*meta*), 130.7 (Ph-*ortho*), 153.6 (Ph-*ipso*)[22]. − ^{19}F NMR (188.3 MHz, C_6D_6): δ = −110.2 (m, 2 F, C_6F_5-*ortho*), −160.4 (m, 1 F, C_6F_5-*para*), −163.2 (m, 2 F, C_6F_5-*meta*). − $C_{64}H_{70}CdF_5KO_8S_2$ (1277.9): calcd. C 60.15, H 5.52, Cd 8.80, F 7.43, K 3.06, S 5.02; found C 59.87, H 5.65, Cd 8.37, F 7.3, K 4.03, S 5.10.

X-ray Crystal Structure Analysis of **3** *and* **4**: Intensity data were measured at 23°C on a Siemens/STOE AED2 diffractometer. Graphite-monochromated MoK_α radiation, ω scans, structure solutions by direct methods[23], refinements on F^2 values (full-matrix least-squares)[24].

A suitable single crystal of **3** was obtained by layering first a small amount of toluene and then *n*-hexane over a solution of the compound in tetrahydrofuran. $C_{99}H_{94}Cd_3F_{15}KO_{10}S_3$, M = 2201.3, pale brown crystal, crystal size 0.65 × 0.53 × 0.27 mm, monoclinic, space group $P2_1/c$, a = 25.464(3), b = 14.248(2), c = 28.421(4) Å, β = 104.40(3)°, V = 9988(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.464 gcm^{-3}, F(000) = 4456, μ(MoK_α) = 0.82 mm^{-1}. 11954 reflections collected, intensity variation during data collection: −24%, $3° \leq 2\Theta \leq 43°$, $0 \leq h \leq 26$, $0 \leq k \leq 14$, $-29 \leq l \leq 28$, empirical absorption correction, T_{min} = 0.3081, T_{max} = 0.4240. 11472 independent reflections (R_{int} = 0.0407) of which 11470 were used in the final refinement, 802 parameters, S (on F^2) = 1.022, $R1$ (all data) = 0.1415, $wR2$ (all data) = 0.1699, $R1$ [$I > 2\sigma(I)$] = 0.0678, max. and min. electron density in final difference map: +0.52 and −0.42 eÅ^{-3}. Each of the THF molecules was assumed to be disordered on two positions, occupied in the ratio of 3:2. A common isotropic U value was refined for the non-hydrogen atoms of each individual position. Anisotropic displacement parameters were refined for all other non-hydrogen atoms, except the C atoms of the trityl groups. All H atoms were included on idealized positions.

A single crystal of **4**, suitable for X-ray structure determination, was grown by layering *n*-hexane over a dilute solution of the compound in tetrahydrofuran. $C_{64}H_{70}CdF_5KO_8S_2$, M = 1277.9, pale yellow crystal, crystal size 0.76 × 0.53 × 0.46 mm, monoclinic, space group $C2/c$, a = 20.230(2), b = 13.897(1), c = 22.512(2) Å, β = 101.65(1)°, V = 6198.6(9) Å^3, Z = 4, $\rho_{calcd.}$ = 1.369 gcm^{-3}, F(000) = 2648, μ(MoK_α) = 0.55 mm^{-1}. 5721 reflections collected, intensity variation during data collection: −15%, $3.6° \leq 2\Theta \leq 48°$, $0 \leq h \leq 23$, $0 \leq k \leq 15$, $-25 \leq l \leq 25$, no absorption correction. 4868 independent reflections (R_{int} = 0.0312) of which all were used in the final refinement, 372 parameters, S (on F^2) = 1.107, $R1$ (all data) = 0.0977, $wR2$ (all data) = 0.1098, $R1$ [$I > 2\sigma(I)$] = 0.0510, max. and min. electron density in final difference map: +0.50 and

-0.32 eÅ^{-3}. Anisotropic displacement parameters were refined for the non-hydrogen atoms, except in the THF ligand, which was assumed to be disordered on three equally occupied positions. A common isotropic U value was refined for the non-hydrogen atoms of each individual position. A total of 30 restraints (DFIX instructions) were used to generate idealized geometries for the THF molecules. For practical reasons, an envelope conformation was chosen with metrical data (C−O 1.43, C−C 1.54 Å; C−O−C 106, O−C−C and C−C−C 104°) close to the values found for free THF[25]. All H atoms were included on idealized positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100805. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor *Manfred Weidenbruch* on the occasion of his 60th birthday.

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