Self-assembly of Single-(Cd_4O_4) and Double-cube (Cd_7O_8) and Stellated-octahedron (Cd_6O_8) [$Cd_n(C_6F_5)_{2n-p}(moe)_p$] Complexes (moe = 2-methoxyethanolate) and the X-Ray Crystal Structures of [*n,p*] = [4,4], [7,8] and [6,8]

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Depending on the relative amount of $MeOCH_2CH_2OH$ (Hmoe), the partial alcoholysis of [$Cd(C_6F_5)_2$] affords the complexes [$Cd_4(C_6F_5)_4(moe)_4$], [$Cd_7(C_6F_5)_6(moe)_8$] and [$Cd_6(C_6F_5)_4(moe)_8$] which have {$Cd_4(\mu_3\text{-}OR)_4$}$^{4+}$, {$Cd_7(\mu_3\text{-}OR)_8$}$^{6+}$ and {$Cd_6(\mu_3\text{-}OR)_8$}$^{4+}$ cores, respectively; several further multinuclear Cd^{2+}–$C_6F_5^-$–moe^- species appear in the CI-mass spectra of these complexes.

There is a growing interest in neutral metal complexes such as [$Cd_9(OCH_2CH_2OMe)_{18}$],[1] [$Cd_2\{OC(Bu^t)(CH_2OPr^i)_2\}_4$][2] and [$Cd_{32}S_{14}(SPh)_{36}(dmf)_4$][3] containing Cd–O and Cd–S cores. This stems in part from potential industrial applications of this class of compounds, *e.g.* in the preparation of thin chalcogenide layers by the MOCVD technique[4] or as quantum dots.[5]

Alcoholysis of a metal organyl or amide is the standard reaction method for the preparation of molecular alkoxides. We found that from such a reaction, namely the protolysis of bis(pentafluorophenyl)cadmium[6] with 2-methoxyethanol ($MeOCH_2CH_2OH$, Hmoe), at least four heteroleptic intermediates could be isolated [eqn. (1)].

$$n\,[\mathrm{Cd(C_6F_5)_2}] + p\,\mathrm{Hmoe} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{room temp.}} [\mathrm{Cd}_n(\mathrm{C_6F_5})_{2n-p}(\mathrm{moe})_p] + p\,\mathrm{C_6F_5H} \tag{1}$$

The product complexes, abbreviated as [*n,p*], are [$Cd_4(C_6F_5)_4(moe)_4$] {[4,4]}, [$Cd_7(C_6F_5)_6(moe)_8$] {[7,8]} and [$Cd_6(C_6F_5)_4(moe)_8$] {[6,8]}. The fourth product has composition $Cd_6(C_6F_5)(moe)_{11}$ and was obtained at a [$Cd(C_6F_5)_2$]: Hmoe mole ratio of 1 : 2.20 instead of the expected complex [$Cd_9(moe)_{18}$] which was prepared from [$Cd\{N(SiMe_3)_2\}_2$] by Hubert-Pfalzgraf and coworkers.[1] Complexes [4,4], [7,8] and [6,8] formed at reactant ratios of 1 : 0.80, 1 : 1.04 and 1 : 1.32, respectively,† were characterized by single-crystal X-ray diffraction.‡ The outcome of the reaction is solely determined by the relative amounts of [$Cd(C_6F_5)_2$] and Hmoe in the reaction mixture. Hence, this is a case of 'strict' self-assembly according to Lindsey's classification scheme.[8]

Complex [4,4] has a conventional hetero-cubane structure {Fig. 1; *cf.* also the structure of [$Cd_4(C_6F_5)_4(SBu^t)_4$][9]}. A special feature, however, is the coordinated ether O atoms which increase the coordination number of the metal atoms from four to five. The double-cubane complex [7,8] (Fig. 2) is formally a condensation product of two [4,4] complexes. Its central atom Cd(1) has a pure alkoxide O coordination. In contrast to [4,4], the ether O atoms are unevenly distributed between the remaining Cd atoms. The core of the complex [6,8] (Fig. 3) is formed by a spherical $Cd_6(\mu_3\text{-}O)_8$ cage 5.0 Å in diameter. None of the cage atoms are displaced by more than 0.09 Å from the mean spherical surface. The coordination of all ether O atoms to only two of the metal centres leads to the high coordination number of eight of these subsites. The Cd–O_{ether} bond lengths are over a wide range (0.44 Å), and the larger ones are typical of weak (secondary) Cd–O bonds.

For all three complexes the base stabilization by coordination of ether O atoms is obvious. In the absence of these interactions, the two axial Cd atoms of [6,8] would be extremely coordinatively unsaturated. The existence of [$Cd_4(C_6F_5)_4(OR)_4$] cubane-type complexes, however, does

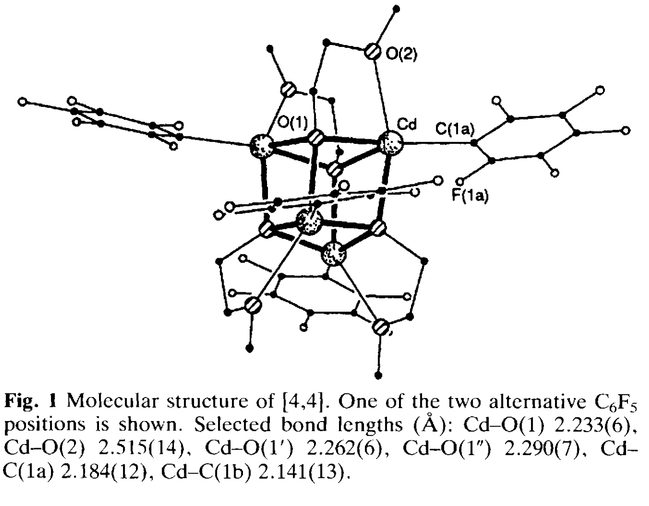

Fig. 1 Molecular structure of [4,4]. One of the two alternative C_6F_5 positions is shown. Selected bond lengths (Å): Cd–O(1) 2.233(6), Cd–O(2) 2.515(14), Cd–O(1′) 2.262(6), Cd–O(1″) 2.290(7), Cd–C(1a) 2.184(12), Cd–C(1b) 2.141(13).

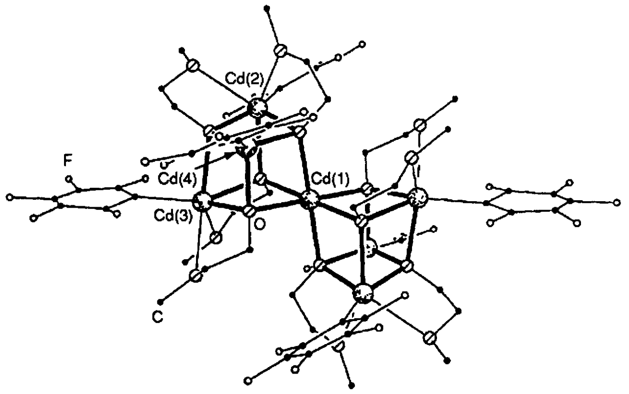

Fig. 2 Molecular structure of [7,8]. Selected bond lengths (Å) with mean values in square brackets: Cd(1)–μ_3-O 2.29(2)–2.33(2) [2.31], Cd(2,3)–μ_3-O 2.25(3)–2.45(2) [2.33], Cd(2,3)–O_{ether} 2.44(2)–2.63(3) [2.54], Cd(2,3)–C_6F_5 2.15(4), 2.21(4) [2.18]; Cd(4)–μ_3-O 2.16(2)–2.27(3) [2.23], Cd(4)–C_6F_5 2.11(3).

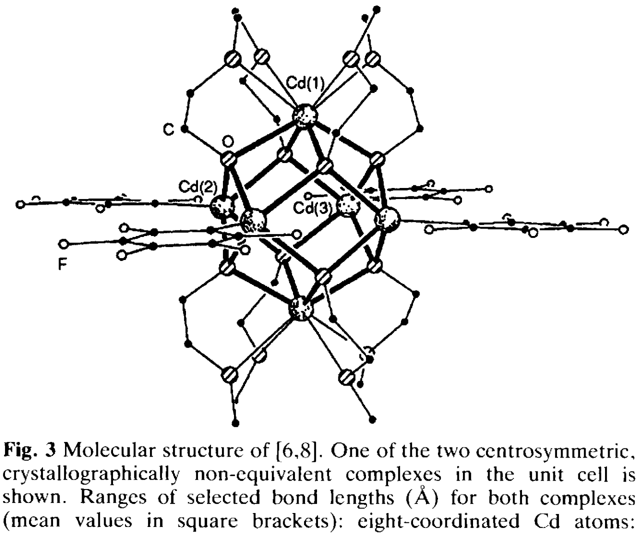

Fig. 3 Molecular structure of [6,8]. One of the two centrosymmetric, crystallographically non-equivalent complexes in the unit cell is shown. Ranges of selected bond lengths (Å) for both complexes (mean values in square brackets): eight-coordinated Cd atoms: Cd–μ_3-O 2.295(4)–2.357(4) [2.32], Cd–O_{ether} 2.459(5)–2.896(6) [2.62]; five-coordinated Cd atoms: Cd–μ_3-O 2.275(4)–2.314(4) [2.30], Cd–C_6F_5 2.196(6)–2.211(6) [2.20].

not depend on additional donors; examples with monofunctional alkoxides (R = Pr^i, 1-adamantyl) will be described elsewhere. The common building block of [4,4], [7,8] and [6,8] is a Cd_3 triangle capped by a μ_3, η^2-moe$^-$ ligand.

The thermolysis of [4,4], [7,8] and [6,8] in a mass spectrometer temporarily results in CI spectra (*iso*-butane) rich in signals of di- to octa-nuclear cadmium complexes. A total of 20 additional Cd^{2+}–$C_6F_5^-$–moe$^-$ species could be identified, *e.g.* $[Cd_3(C_6F_5)_2(moe)_3]^+$ (*m/z* 897) in all spectra and $[Cd_8(C_6F_5)_5(moe)_{10}]^+$ (*m/z* 2486) in the spectrum of [6,8]. The composition of $[Cd_6(C_6F_5)(moe)_{10}]^+$ (*m/z* 1592), another ion found in the MS of [6,8], is closely related to that of the reaction product $[Cd_6(C_6F_5)(moe)_{11}]$ mentioned above.

In conclusion, it has been shown that $C_6F_5^-$ and moe$^-$ are a highly flexible ligand combination with Cd^{2+}. Interestingly, this flexibility only concerns the composition of the complexes and the coordination number of the metal, while the binding modes of the ligands (terminal and μ_3, η^2-bridging, respectively) remain unchanged. Most procedures for the preparation of neutral chalcogen-ligand complexes by protolysis use educt complexes of high reactivity, often the metal bis(trimethylsilyl)amides. From our results, it appears promising to look for less reactive starting materials in order to allow stable heteroleptic intermediates to be formed. This approach points to a search for suitable *combinations* of ligands.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. We also thank Professor S. Pohl for his continuous interest and encouragement, and Mr W. Saak for collection of the diffraction data.

Received, 30th September 1994; Com. 4/06002D

Footnotes

† [4,4], [7,8]·$2CH_2Cl_2$ and [6,8]·$2CH_2Cl_2$ were prepared under an atmosphere of pure nitrogen by addition of Hmoe (2.0, 2.6 and 3.3 mmol, respectively) in CH_2Cl_2 (1–2 ml) to a solution of freshly prepared $[Cd(C_6F_5)_2]$ (1.12 g, 2.5 mmol) in CH_2Cl_2 (3 ml). The colourless, air-sensitive products crystallized at room temp. and were isolated after a few days. Yields: 0.30 g (42%), 0.75 g (90%) and 0.50 g (57%), respectively. Satisfactory elemental analyses were obtained. [7,8]·$2CH_2Cl_2$ and [6,8]·$2CH_2Cl_2$ rapidly effloresce by partial loss of CH_2Cl_2. The compounds are most conveniently identified by small differences in their IR spectra (KBr mulls): [4,4] ν_{max}/cm^{-1} 1501m, 1258w, 950s, 768m, 574m, 422m; [7,8]·$2CH_2Cl_2$ ν_{max}/cm^{-1} 1504m, 1256m, 952s, 766m, 741m (CH_2Cl_2), 575s, 429m; [6,8]·$2CH_2Cl_2$ ν_{max}/cm^{-1} 1501m, 1248m, 948s, 754m, 737s (CH_2Cl_2), 568s, 425m.

‡ *Crystal data* for [4,4]: $C_{36}H_{28}Cd_4F_{20}O_8$, M = 1418.2, tetragonal, space group $I4_1/a$, a = 18.330(4), c = 13.776(3) Å, V = 4628.6 Å^3, Z = 4, D_c = 2.035 g cm^{-3}, μ(Mo-Kα) = 19.3 cm^{-1}, crystal size 0.80 × 0.51 × 0.38 mm, $2\theta_{max}$ = 46°, ω-scans, 3296 measured (1610 independent) reflections, R = 0.047 and R_w = 0.046 from 879 reflections with $I > 2\sigma(I)$, 139 parameters, max, min peak in final Fourier difference synthesis +0.34, −0.27 e Å^{-3}. [4,4] possesses a superstructure with a = 25.921(2), b = 13.785(3), c = 40.988(3) Å, β = 108.43(1)°, space group *Cc* or *C2/c*. This structure was solved in *C2/c* on the basis of appropriate diffraction data, but, due to the weakness of the data set, a satisfactory refinement was not possible.

For [7,8]·$2CH_2Cl_2$: $C_{62}H_{60}Cd_7Cl_4F_{30}O_{16}$, M = 2559.8, triclinic, space group $P\bar{1}$, a = 12.664(3), b = 13.230(3), c = 14.286(4) Å, α = 79.20(1), β = 75.42(1), γ = 66.37(2)°, V = 2112.1 Å^3, Z = 1, D_c = 2.013 g cm^{-3}, μ(Mo-Kα) = 19.7 cm^{-1}, crystal size 0.68 × 0.30 × 0.10 mm, $2\theta_{max}$ = 36° (deterioration of the crystal in the X-ray beam), ω–2θ scans, 3436 measured (2883 independent) reflections, R = 0.078 and R_w = 0.063 fom 1692 reflections with $I > 2\sigma(I)$, 260 parameters, max, min peak in final Fourier difference synthesis +0.86, −0.81 e Å^{-3}.

For [6,8]·$2CH_2Cl_2$: $C_{50}H_{60}Cd_6Cl_4F_{20}O_{16}$, M = 2113.3, triclinic, space group $P\bar{1}$, a = 12.175(2), b = 13.841(3), c = 22.783(5) Å, α = 89.04(1), β = 78.70(2), γ = 67.48(1)°, V = 3470.5 Å^3, Z = 2, D_c = 2.022 g cm^{-3}, μ(Mo-Kα) = 20.7 cm^{-1}, crystal size 1.37 × 0.91 × 0.61 mm, $2\theta_{max}$ = 50°, ω-scans, 12931 measured (12209 independent) reflections, R = 0.041 and R_w = 0.039 from 9450 reflections with $I > 2\sigma(I)$, 865 parameters, max, min peak in final Fourier difference synthesis +0.99, −1.06 e Å^{-3}.

Diffraction data were collected at 23 °C on a Siemens/STOE AED2 diffractometer using Mo-Kα radiation (λ = 0.71069 Å). The structures were solved by direct methods and refined on F values.[7] Empirical absorption corrections (ψ scans) were made for [7,8]·$2CH_2Cl_2$ and [6,8]·$2CH_2Cl_2$. The disordered $C_6F_5^-$ ligand in [4,4] was refined as a rigid group on two positions with bond distances and angles taken from the structure of $[Cd(C_6F_5)_2]$ (ligand 2).[6] Anisotropic thermal parameters were refined for all non-hydrogen atoms except disordered C atoms {[4,4]}, for the Cd atoms only {[7,8]·$2CH_2Cl_2$} and for all non-hydrogen atoms {[6,8]·$2CH_2Cl_2$}, respectively. H-atoms were included on idealized positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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