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Tripyrrinatocadmium Complexes: Enforcing Supramolecular Aggregation by a Large Ion

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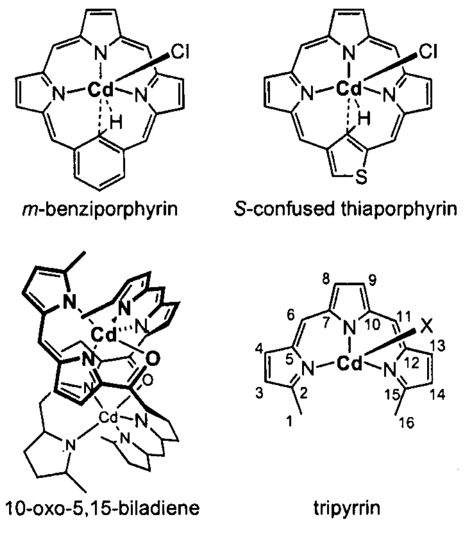
A newly developed method for the preparation of free base tripyrrin ligands HTrpy by cyanide-promoted demetalation of nickel chelates TrpyNiNCO was used in order to explore the chemistry of cadmium tripyrrins TrpyCdX with a variety of anionic co-ligands X. The introduction of the large Cd^{II} ion into the tripyrrin N_3 coordination site was accomplished by the use of cadmium acetate as the metal precursor. Ligand exchange experiments using sodium salts of different anions disclose a marked tendency for pentacoordination, which is achieved either by the formation of chelates or of 1D coordination polymers that form as a consequence of the size of the central metal. The attempted introduction of chlorido, iodido, or cyanato ligands thus leads mainly to decomposed material, while the use of 1,1,1-trifluoracetylacetonate, salicylate, and acetate ligands results in stable, pentacoordinate and monomeric complexes with the external ligand bound as a four- or six-membered *O*,*O*-chelate ring. With the pseudohalogenido ligands thiocyanate, selenocyanate, and azide as well as with the weakly coordinating trifluoroacetate 1D coordination polymers with a variety of chain structures were obtained and investigated by X-ray diffraction studies. Interestingly $TrpyCdN_3$ is present in the crystal as a coordinatively and hydrogen-bonded methanol adduct with a dimeric repeating subunit.

Introduction

The Cd^{II} ion has only recently been recognized as a useful species in porphyrinoid chemistry. In a series of ring-exchanged porphyrinoids like *m*-benziporphyrin, *S*-confused thiaporphyrin and the like (Figure 1) the spin-active nuclei of ^{111}Cd and ^{113}Cd (I = 1/2) have been used to detect unusual metal–ligand interactions through the observation of ^{1}H-Cd and ^{13}C-Cd scalar couplings (so-called "through-space couplings") in the NMR spectra.[1] This approach makes the Cd^{II} ion a unique probe, that allows the direct spectroscopic investigation of nonbonding metal–ligand interactions for diamagnetic ions. Cadmium complexes of porphyrins are also known,[2] but have only scarcely been used[3] due to their pronounced solvolytic lability. The problem appears to be the size of the Cd^{II} ion, which is too large to allow a proper adaptation of the porphyrin macrocycle. This results in largely domed structures with open sites for solvent attack. As has been shown in 1998 flexible open-chain tetrapyrroles with more than four donor atoms are much more effective in providing a suitable coordination sphere for cadmium, which obviously prefers a coordination number of larger than four in a porphyrinoid environment (Figure 1).[4]



m-benziporphyrin

S-confused thiaporphyrin

10-oxo-5,15-biladiene

tripyrrin

Figure 1. Selected tri- and tetrapyrrolic cadmium chelates.

The tripyrrin ligand HTrpy is formally derived from the macrocyclic parent porphyrin by the loss of one of the four C_4N rings.[5] Chemically, however, the Trpy ligand differs largely from the porphyrin and from other macrocyclic porphyrinoids with respect to ligand stability and the open *cis*-situated coordination site at the central ion. The presence of two terminal methyl moieties, which is currently one of the synthetic limitations of tripyrrin ligand synthesis, leads to an effective shielding of the one coordination site situated in the N_3M-plane of a given complex.[6] Earlier studies

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have shown, that as a result of this steric constraint palladium(II) complexes of Trpy ligands are always distorted from a square-planar geometry[7] and that tetracoordinate tripyrrinatonickel(II) complexes display a sterically induced HS ground state despite an intermediately strong ligand field.[8]

The presence of two terminal methyl groups at the tripyrrin ligand framework limits the maximum coordination number of all metallotripyrrins described so far to five. The association of a fifth donor L to a four-coordinate compound TrpyMX can in principle occur from either side of the tripyrrin plane, resulting in two different coordination geometries **A** and **B** (Figure 2). In this regard tripyrrins differ largely from the structurally similar, but more flexible bis(arylimino)isoindolines (BAI), which have been shown in the recent past to adopt nonplanar conformations and non-meridonal tridentate binding modes in several instances.[9] Complexes of type **A** are of particular interest due to their propensity to form 1D- and 3D coordination polymers with a large structural variety. However, the number of ions that have been shown to form five-coordinate metallotripyrrins is almost limited to one, i.e. Ni^{II}.[10] In addition, two examples of mononuclear pentacoordinate palladium(II)-tripyrrin complexes and one example for an extremely labile pentacoordinate cobalt(II)-tripyrrin complex have been unravelled.[11] In this contribution we describe our successful attempt to employ the large ion Cd^{II} in order to enforce the formation of 1D coordination polymers from TrpyCd subunits.

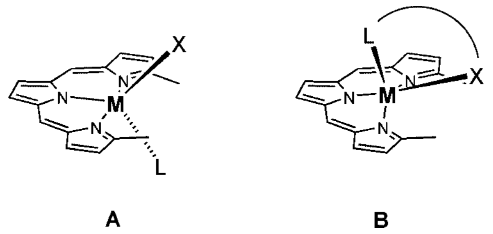
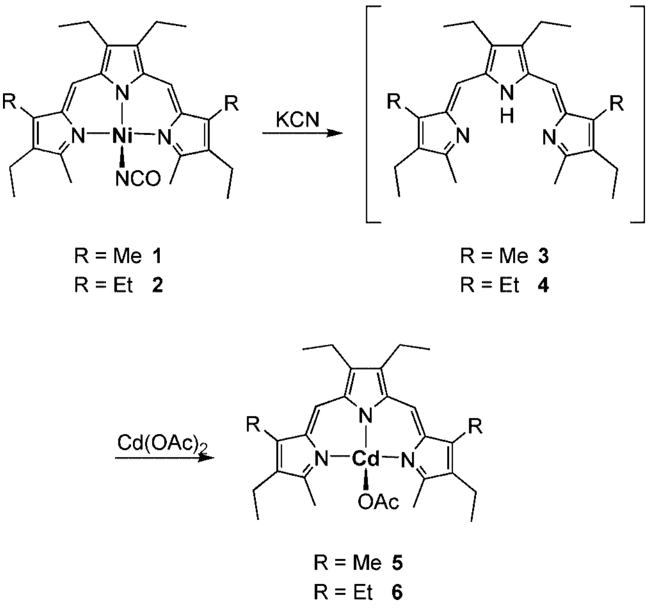


Figure 2. Generalized structures **A** and **B** for pentacoordinate metallotripyrrins.

Results and Discussion

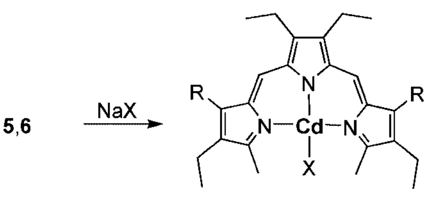
Preparation and spectroscopic characterization. During our studies on ligand exchange procedures of TrpyNi complexes we recently realized that the attempted ligand exchange of the isocyanates TrpyNiNCO **1** and **2**[10a] with excess cyanide results in the demetalation of the chelate complexes, which is indicated by an immediate color change from dark green to red. The red solutions of the putative free base tripyrrins **3** and **4**, which were obtained after washing with water and phase separation, proved very unstable over time. The advent of the free base ligands **3** and **4**, however, opens the desired possibility to obtain more sensitive tripyrrin complexes like TrpyCdX, which are unavailable by other means. For the metalation of the free base tripyrrins a two-phase system with the ligand in the ethereal phase and $Cd(OAc)_2$ in the aqueous one was applied. Some methanol was added to ensure the interpenetration of the two layers and thus to enhance the metalation rate. No additional base is necessary to drive the metalation to completion. Since the removal of the solvent often leads to the decomposition of sensitive metallotripyrrins the product solutions of **5** and **6** were used directly in ligand exchange reactions without further purification. Only for TrpyCdOAc **5** an attempt to isolate and characterize the compound was undertaken (Scheme 1).



Scheme 1. Preparation of tripyrrinatocadmium complexes **5** and **6** via free base tripyrrins **3** and **4**.

The composition TrpyCdOAc was confirmed for the new complex **5** by elemental analysis and by EI mass spectrometry, which shows two peaks at *m*/*z* = 561 and 501 for the M^+ and $[M – OAc]^+$ ion, respectively. The UV/Vis spectrum is dominated by two absorptions at 350 and 650 nm from ligand-based transitions and resembles those of other metallotripyrrins.[10,11] Spectroscopically, the new complex shows A_2X_3 systems for two chemically distinct ethyl substituents in addition to four singlets for the methyl groups at C-2,15 ($\delta = 2.50$ ppm), C-4,13 ($\delta = 2.20$ ppm) and at the acetate ($\delta = 1.87$ ppm) as well as for the *meso* protons at C-6,11 ($\delta = 6.86$ ppm). The spectrum is almost indistinguishable from those of TrpyZnX species[12] and contains no information for the coordination mode of the acetato ligand. From IR data the acetate coordination can be assigned to a bidentate binding mode. The ν_{CO} stretching band is found at 1553 cm^{-1} and therefore below the value for the free acetate ion. For monodentate acetate ligands stretching frequencies of >1600 cm^{-1} are typical.[13] TrpyCdOAc **5** can therefore be regarded as a pentacoordinate species, presumably of type **B**.

Ligand exchange reactions were carried out on **5** and **6** under biphasic standard conditions using different monoanionic halide, pseudohalide, and *O*,*O*-chelate ligands as their sodium salts (Scheme 2). The use of chlorido-, bromido-, iodido-, and cyanato ligands resulted in labile material which decomposed to a large extent upon the attempted isolation. For X = NCS, NCSe, N_3, sal, 1,1,1-trifluoroacetylacetonate (acac^F), and trifluoroacetate (OAc^F), however, pure complexes TrpyCdX **7**–**12** were obtained in good yield (the azido derivative **9** was obtained as a methanol adduct) and characterized by means of elemental analyses and mass spectra.



X	R	
	Me	Et
NCS	7	
NCSe	8	
N_3	9	
acac^F	10	
sal		11
OAc^F		12

Scheme 2. Anion metathesis reactions on tripyrrinatocadmium complexes **5** and **6**.

All new complexes form violet crystals with a metallic sheen. In solution intense green colors are observed throughout. The solubility, however, differs strongly with the anionic ligand. The pseudohalide derivatives TrpyCdNCS **7**, TrpyCdNCSe **8**, and TrpyCdN_3(MeOH) **9** are almost insoluble in nondonor solvents, while the compounds with the *O*,*O*-chelate ligands TrpyCdacac^F **10**, TrpyCdsal **11**, and TrpyCdOAc^F **12** dissolve readily in, for example, dichloromethane. From UV/Vis data **7**–**12** can be divided into two groups. Thiocyanate **7** and selenocyanate **8** yield optical spectra with two major maxima at about 345 and 630 nm, while the *O*,*O*-chelated species **10**–**12** and the methanol-azido compound **9** yield spectra similar to that of the acetato complex **5** with maxima at about 350 and 650 nm. ^{1}H and ^{13}C NMR spectra of **7**–**12** are also very similar to the one discussed in detail for **5** and differ mainly by the signals for the respective anionic coligands. Characteristic shifts for the coordination number or type were not found for the diamagnetic cadmium chelates (Figure 3).

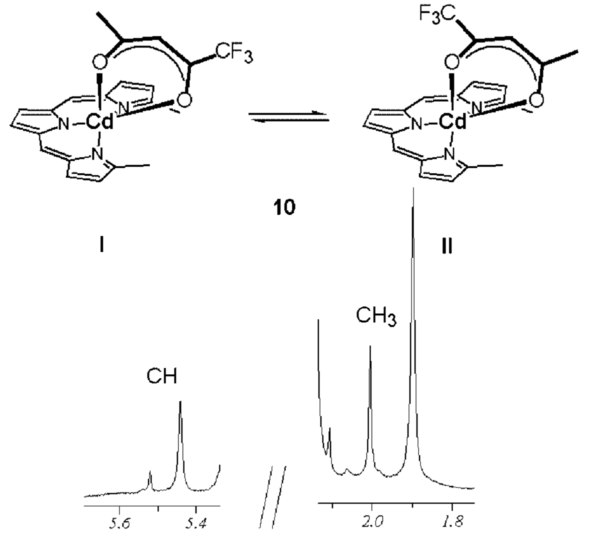


Figure 3. Details of the ^{1}H NMR spectra of TrpyCdacac^F (**10**) (230 K, CD_2Cl_2) and schematic representations of isomers I and II (β-alkyl groups omitted).

Dynamic behavior was observed in the proton NMR spectra of the 1,1,1-trifluoroacetoacetato derivative TrpyCdacac^F **10**. At ambient temperature, the resonance signals of the acac^F ligand appear extremely broadened and split into two pairs of singlets with a ratio of 5:2 at low temperature (Figure 3). At 230 K, the peaks for the major form are found at 1.90 (CH_3) and 5.44 (CH) ppm, while those for the minor form are recorded low field at $\delta = 2.00$ and 5.52 ppm. This dynamic process of **10** can be interpreted in terms of the interconversion of two isomers I and II (Figure 3). The attempted assignment of I and II to major and minor form by a ROESY experiment, however, failed.

IR spectroscopy is a particularly well-suited tool in order to determine the binding mode (i.e. terminal or bridging) of the anion in complexes with pseudohalide ligands, and thus to assign the degree of complex association. Typical of monomeric omplexes with *N*-bound terminal NCS and NCSe ligands are ν_{as} vibrations with wavenumbers well below 2100 cm^{-1}.[13] For TrpyCdNCS (**7**) and TrpyCdNCSe (**8**), however, the band for this vibration is found at 2103 and 2115 cm^{-1}, respectively. In combination with the low solubility of these species this finding points to the presence of bridging pseudohalide ligands for **7** and **8** and thus of coordination polymers in the solid state. The thiocyanate ion has frequently been reported as a bridging ligand in coordination polymers,[14,15] as has been for the homologous selenocyanate, although reports about the use of this nonconventional pseudohalide are rather rare.[15,16]

In the IR spectra of the azido complex TrpyCdN_3(MeOH) (**9**) two equally intense bands are found in the region for the N_3 vibrations at 2090 and 2067 cm^{-1}. As before these values are higher than those expected for complexes with terminal monodentate azido ligands. In addition, the splitting into two bands indicates, that the azide is situated in a bridging coordination mode. From this data it remains open, whether an *end-on* ($\mu_{1,1}$) or an *end-to-end* ($\mu_{1,3}$) coordination is realized for **9**.[17] The ν_s bands at about 1300 cm^{-1}, which are characteristic for the distinction between these two binding modes, overlap severely with bands from the tripyrrin backbone and cannot be assigned unambiguously. For sterical reasons, however, the *end-to-end* ($\mu_{1,3}$) coordination is favored and thus the formation of a polymeric structure of TrpyCdN_3(MeOH) (**9**).

X-ray crystallographic characterization. Single crystal X-ray diffraction studies were undertaken on suitable crystals of the pseudohalide species TrpyCdNCS (**7**), TrpyCdNCSe (**8**), and TrpyCdN_3(MeOH) (**9**) as well as on the *O*,*O*-chelate complexes TrpyCdacac^F (**10**), TrpyCdsal (**11**), and TrpyCdOAc^F (**12**) and will be discussed below. Details for the structure solutions and refinements are summarized in Table 1.

TrpyCdNCS and TrpyCdNCSe crystallize isotypically by slow evaporation of respective solutions in toluene/methanol in the monoclinic system, space group *C*2/c, with $Z = 4$ and very similar unit cell metrics [**7**: $a = 26.972(3)$, $b = 11.7933(9)$, $c = 18.827(2)$ Å, $\beta = 95.564(13)°$; **8**: $a = 27.073(2)$, $b = 11.9547(9)$, $c = 18.7485(16)$ Å, $\beta = 95.391(10)°$]. In both cases one half molecule of a severely

Table 1. Crystal data and structure refinement for compounds **7**–**12**.

	7·0.5 C_7H_8	**8**·0.5 C_7H_8	**9**	**10**	**11**·0.5 CH_2Cl_2	**12**
Formula	$C_{61}H_{68}Cd_2N_8S_2$	$C_{61}H_{68}Cd_2N_8Se_2$	$C_{54}H_{76}Cd_2N_{12}O_2$	$C_{31}H_{39}CdF_3N_3O_2$	$C_{67}H_{80}Cd_2Cl_2N_6O_6$	$C_{30}H_{38}CdF_3N_3O_2$
M_r	1202.16	1295.96	1150.07	655.05	1361.09	642.03
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a [Å]	26.972(3)	27.073(2)	11.2992(16)	11.1577(8)	11.3946(4)	13.433(3)
b [Å]	11.7933(9)	11.9547(9)	12.5623(15)	11.9654(8)	16.1260(5)	10.076(2)
c [Å]	18.827(2)	18.7485(16)	19.676(2)	12.2531(8)	17.7046(6)	22.511(5)
α [°]	90	90	95.312(14)	101.419(6)	90	90
β [°]	95.564(13)	95.391(10)	93.744(15)	107.581(5)	106.589(3)	99.16(3)
γ [°]	90	90	92.689(16)	97.061(6)	90	90
Z	4	4	2	2	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.340	1.425	1.378	1.451	1.448	1.418
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Monochromator	graphite	graphite	graphite	graphite	graphite	graphite
Temperature [K]	193(2)	193(2)	193(2)	193(2)	193(2)	193(2)
Data collection	ϕ-scan	ϕ-scan	ϕ-scan	ω-scan	ω-scan	ϕ-scan
Θ range [°]	2.14–25.35	1.86–26.06	1.81–25.35	1.80–26.19	1.70–26.13	1.83–26.11
Measured reflections	21904	23525	26093	21357	65693	23416
Indep. reflections[a]	3134	3207	4625	5656	5797	4333
Absorption coefficient	0.827	1.952	0.818	0.779	0.824	0.775
Solution method[b]	direct	direct	direct	Patterson	direct	direct
Final R_1 value	0.0281	0.0317	0.0605	0.0697	0.0640	0.0464

[a] $I > 2\sigma(I)$. [b] All structures were solved using "SHELXS, Program for Crystal Structure Determination"[18] and refined with "SHELXL, Program for Crystal Structure Refinement".[19]

disordered toluene molecule per formula unit is present in the cell. As expected from the IR spectroscopic results both compounds indeed form 1D coordination polymers (Figure 4; Table 2).

TrpyCdNCS (**7**) and TrpyCdNCSe (**8**) form type **A** metallotripyrrins in the solid state. The coordination environment of the Cd^{II} ion in 7 and **8** can be assigned to distorted trigonal bipyramids with N1 and N3 in the apices and N2, N4, and S or Se, respectively, in the equatorial positions. The assignment is based mainly on the N–Cd–N and N–Cd–S/Se angles which deviate less than 11° from the ideal 90°, 120°, or 180° for this polyhedron. The combination of the large ionic radius of cadmium and the coordination number of 5 results in the longest M–N_{Trpy} bonds of 2.217–2.274 Å observed so far in the chemistry of the tripyrrins. The typical relation, that the central M–N2 bond is shorter than the terminal N1–M and N3–M bonds, is found for type **A** cadmium tripyrrins, too. The tripyrrin backbones C2–C15 of both compounds display slight helical distortions, which appears necessary in order to accommodate the large cadmium atom in the ligand N,N,N planes [deviation ("doming") for **7**: 0.0799(2), for **8**: 0.1545(3) Å]. As a result the methyl termini C1 and C16 are as far apart from each other as 5.570(6) (**7**) and 5.596(6) Å (**8**) and leave much space for the binding of N4 and S/Se. In fact, despite the size of the S or Se donor the arrangement at the open sites of the TrpyCd moieties is almost unstrained, and the distance between the N4 and S/Se donor on one hand and the terminal methyl groups C1, C16 on the other undercuts the sum of the van der Waals distances by only 4.5 (**7**) and 5.8% (**8**). For comparison, this value is of the same magnitude as for most tetracoordinate metallotripyrrins, and is increased to almost 20%, if the metal enforces a square-planar coordination mode like in TrpyNiCN.[10a]

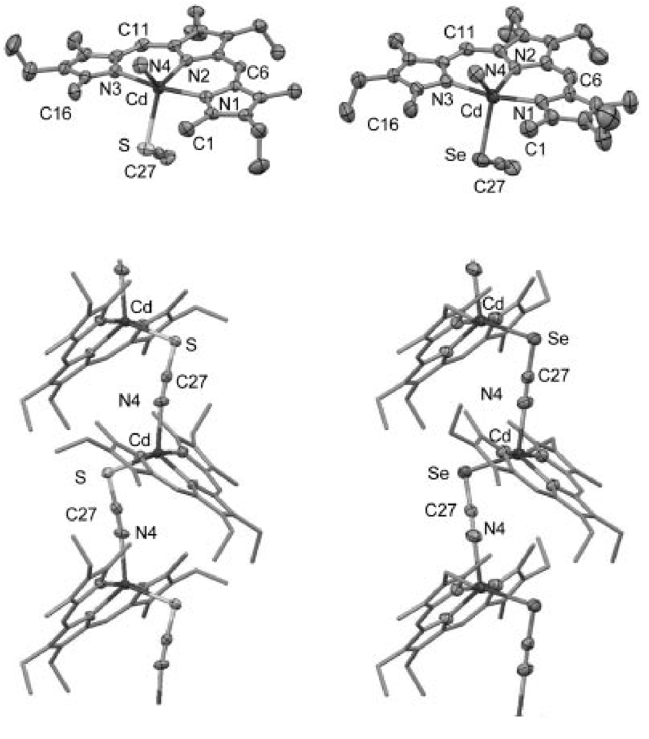


Figure 4. Repeating units of TrpyCdNCS (**7**) (top left) and TrpyCdNCSe (**8**) (top right) from X-ray crystallographic analyses, and representation of the isotypical single chain arrangements of **7** (left) and **8** (right; ellipsoids set at 50% probability; hydrogen atoms omitted for clarity).

As mentioned above, **7** and **8** form isotypical 1D coordination polymers that propagate in the direction of the crystallographic *b* axis. The TrpyCd plates are organized with a Cd···Cd distance of 6.184 (**7**) and 6.230 Å (**8**), and arrange

Table 2. Selected bond lengths [Å] and angles [°] for complexes TrpyCdNCS (**7**), TrpyCdNCSe (**8**), and TrpyCdN_3(MeOH) (**9**).

	7·0.5 C_7H_8	**8**·0.5 C_7H_8	**9**	
			Subunit I (Cd1)	Subunit II (Cd2)
M–N1	2.266(3)	2.270(3)	2.259(7)	2.248(7)
M–N2	2.220(3)	2.217(3)	2.250(6)	2.219(6)
M–N3	2.274(3)	2.268(3)	2.239(7)	2.277(7)
M–D1[a]	2.309(2)	2.323(4)	2.357(8)	2.295(7)
M–D2[a]	2.6667(11)	2.7369(6)	2.295(7)	2.346(7)
N1–M–N2	85.87(9)	86.03(12)	86.0(2)	86.2(2)
N1–M–N3	171.16(9)	169.16(11)	171.7(2)	168.9(2)
N1–M–D1[a]	90.23(10)	89.68(13)	87.3(3)	102.0(3)
N1–M–D2[a]	93.52(7)	95.42(8)	90.5(3)	89.2(3)
N2–M–N3	86.12(9)	85.93(12)	85.7(2)	86.8(2)
N2–M–D1[a]	123.49(10)	122.47(12)	125.3(2)	133.5(3)
N2–M–D2[a]	121.49(7)	123.46(7)	122.4(3)	118.7(2)
N3–M–D1[a]	91.06(10)	88.51(13)	96.9(3)	89.1(3)
N3–M–D2[a]	93.86(7)	95.08(8)	94.5(2)	86.6(2)
D1–M–D2[a]	115.01(8)	114.06(9)	111.9(3)	107.2(3)
C1···C16	5.570(6)	5.596(6)	5.597(13)	5.613(14)
C1···D1	3.454(5)	3.362(5)	3.498(13)	3.595(13)
C1···D2	3.701(4)	4.002(4)	3.412(13)	3.569(13)
C16···D1	3.380(5)	3.430(6)	3.508(12)	3.342(11)
C16···D2	3.940(4)	3.769(4)	3.690(12)	3.476(13)
ΔvdW/%[b]	–4.5	–5.8	–3.0	–5.9
M···Ct(N_3)[c]	0.0799(2)	0.1545(3)	0.0154(7)	0.1807(7)

[a] D1 = N4 for **7** and **8**, N9 for **9-I** or O1 for **9-II**; D2 = S for **7**, Se for **8**, N10 for **9-I**, or N7 for **9-II**. [b] Difference between the C1···D1/2 or C16···D1/2 distance and the sum of the van der Waals radii of D1/2 and the closest terminal methyl group. [c] Displacement of the metal ion from the *N*,*N*,*N* plane of the tripyrrin ligand (doming).

almost vertical with an angle of 97.2 (**7**) and 93.4° (**8**) towards each other. This arrangement is a result of the size (NCS: 2.805; NCSe: 2.948 Å) and binding angles Cd–N4–C27 and Cd–S/Se–C27 of the almost linear pseudohalide ligands (NCS: 177.86; NCSe: 176.84°). As depicted in Figure 4, the coordination of the pseudohalide ligand via the *N*-donor end is rather straight with 166.98 for **7** and 169.42° for **8**, while the chalcogeno donors coordinate at angles as steep as 98.61 (**7**) and 94.14° (**8**). This relaxed arrangement still allows a tight intrastrand packing of the monomers, with minimum distances between methyl carbon atoms of one unit and the sp^2 system of the next of 3.283 (7) and 3.254 Å, and without losing the rather weak Cd–S and Cd–Se coordination.

The pillars consisting of the 1D polymeric strands of **7** and **8** pack more tightly in the crystallographic *c* than in the *a* direction, forming layers of pillars with interdigitated alkyl groups in the solid state. These layers are glued together by disordered toluene molecules that occupy the clefts and thus stabilize the structures of **7** and **8** (Figure 5).

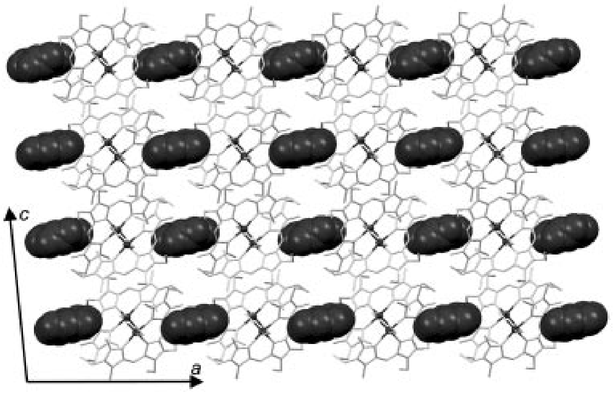


Figure 5. View down the polymeric chains (crystallographic *b* axis) of TrpyNCS (**7**) (capped sticks with balls for the Cd^{II} ions, bright) and representation of the layered structure from alternating pillars of **7** and disordered toluene solvent molecules (space-fill, dark; hydrogen atoms omitted throughout).

The azido ligand deviates from the above pseudohalides by a reduced size. This change in metrics leads to a different solid-state arrangement for **9** and to the necessity to introduce methanol into the coordination of the cadmium ion. After crystallization of freshly prepared TrpyCdN_3 from a toluene/methanol mixture the 1D coordination polymer **9** was obtained, which displays chains of methanol and H-bridge linked TrpyCdN_3 dimers. The chain structure of **9**, a detailed view of the dimeric building block and a representation of the layer-like structure formed by the individual chains are presented in Figure 6. Crystallographic data for **9** and selected molecular parameters can be found in Table 1 and Table 2.

The dinuclear $(TrpyCd)_2N_3$ fragment of the coordination polymer **9** consists of two nonequivalent cadmium tripyrrin units TrpyCd1 and TrpyCd2. In order to adapt sterically to the voluminous Cd^{II} ions the tripyrrin ligands of both TrpyCd units show a slight helical distortion known as "ruffling" in porphyrin chemistry[20] with mean deviations from planar $C_{14}N_3$ frameworks of 0.105 and 0.089 Å for TrpyCd1 and TrpyCd2, respectively. The coordination geometry at the cadmium ions can be described in both cases as distorted trigonal bipyramidal with N1,N2 and N4,N6

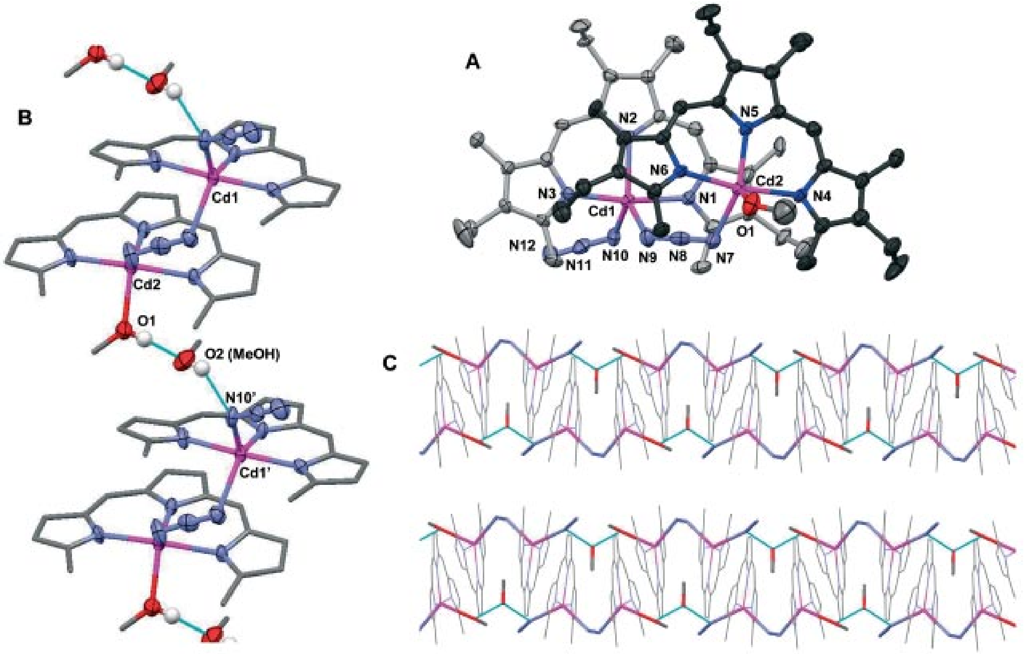


Figure 6. Presentation of the dimeric asymmetric unit (**A**, ellipsoids at 50% probability), the MeOH and H-bond initiated chain formation (**B**, ball-and-stick representation) and the sheet structure (**C**) of coordination polymer $[\mathrm{TrpyCdN_3(MeOH)}]_n$ (**9**) [hydrogen atoms (A–C) and β-alkyl substituents (B,C) omitted for clarity].

in the apical positions, and with N2,N9,N10 and N5,N7,O1 in the equatorial ones. The deviation from an ideal geometry is particularly large for the TrpyCd2 subunit, where angles N7–Cd2–O1 and N4–Cd2–N6 are found at 107.2(3) and 168.9(2)° instead of the ideal 120 and 180°, respectively. Cd1 and Cd2 are bridged by a linear $\mu_{1,3}$ azido ligand [N7–N8–N9: 178.6(9)°], which coordinates to both metal ions in a bent fashion [Cd1–N9–N8: 118.2(6)°, Cd2–N7–N8: 116.2(5)°] and with a torsion Cd1–N9–N7–Cd2 of 75.2(5)°. The Cd–N bonds to the $\mu_{1,3}$ azido ligand are longer for Cd1–N9 than for Cd2–N7 [2.356(8) vs. 2.294(8) Å], which results in slightly asymmetric N–N bonds within the azide anion of N7–N8: 1.215(12) and N8–N9: 1.192(12) Å. The mean planes of the $C_{14}N_3$ frameworks of the tripyrrin subunits are arranged almost coplanar with an angle of 13.57(11)°, and are rotated against each other by 14.4(2)° as indicated by the N2–Cd1–Cd2–N5 torsion angle. The cadmium ions Cd1 and Cd2 of the dimeric unit are separated by 5.2139(12) Å.

A second azido ligand is coordinated to Cd1 with a Cd1–N10 distance of 2.296(8) Å and a Cd1–N10–N11 angle of 120.1(6)°. Cd2, on the other hand, is coordinated to the oxygen atom O1 of a methanol molecule as the fifth donor in a distance of 2.356(7) Å. The N10- and O1′ atoms of neighboring dimeric fragments are connected to each other by H-bonds to a second molecule of methanol at O1′–O2 and O2–N10 distances of 2.623(8) and 2.748(8) Å, respectively. This H-bond network results in the formation of a 1D-coordination polymer (**B** in Figure 6) with the Cd atoms of neighboring dimers Cd1 and Cd2′ situated 8.154(6) Å apart from each other. From a structural point-of-view the second azido anion N10N11N12 should be assigned as a $\mu_{1,1}$ bridging ligand rather than as a terminal azide. As for **7** and **8** before the single chains of the 1D coordination polymer **9** organize to 2D sheets in the crystal lattice, but in this case without interlayered solvent (**C** in Figure 6).

From a dichloromethane/*n*-hexane solution a single crystal of **10** was grown. The X-ray crystallographic analysis proofs the chelate character of the acac^F ligand in the solid state (Figure 7). From the possible isomers only form I (see Figure 3) is present in the crystal. One of the six ethyl groups as well as the CF_3 group of the acac^F ligand were found disordered and treated as such in the structure refinement. Selected molecular parameters of **10** are summarized in Table 3.

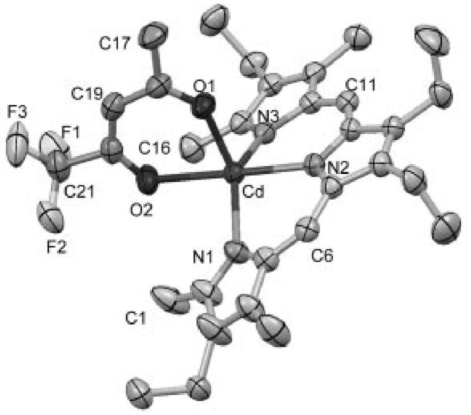


Figure 7. Molecular structure of TrpyCdacac^F (**10**) (ellipsoids at 50% probability; hydrogen atoms omitted for clarity).

The crystallographic analysis identifies **10** as a monomeric molecule of type **B** with a κ^2 coordinated acac^F li-

Table 3. Selected bond lengths [Å] and angles [°] for complexes TrpyCdacac^F (**10**), TrpyCdsal (**11**), and TrpyCdOAc^F (**12**).

	10	**11**	**12**
M–N1	2.2592(18)	2.221(4)	2.263(3)
M–N2	2.2104(16)	2.199(3)	2.226(3)
M–N3	2.2427(17)	2.213(4)	2.260(3)
M–O1	2.2873(15)	2.323(4)	2.263(3)
M–O2	2.2613(16)	2.418(4)	2.346(3)
N1–M–N2	83.85(6)	86.95(14)	86.37(12)
N1–M–N3	140.13(6)	142.94(14)	171.85(12)
N1–M–O1	116.12(6)	102.22(14)	91.76(13)
N1–M–O2	92.75(7)	98.80(14)	91.70(11)
N2–M–N3	86.24(6)	86.09(13)	87.18(12)
N2–M–O1	92.63(6)	104.25(13)	133.86(13)
N2–M–O2	169.78(6)	159.41(13)	130.37(12)
N3–M–O1	102.82(6)	114.77(14)	96.30(13)
N3–M–O2	102.37(7)	100.36(13)	88.69(12)
O1–M–O2	80.18(6)	55.26(12)	95.76(11)
X–O1[a]	1.243(3)	1.253(6)	1.255(5)
Y–O2[a]	1.253(3)	1.274(6)	1.206(5)
X–Z[a]	1.422(3)	1.484(7)	1.536(6)
Y–Z[a]	1.364(3)		
C1···C16	5.023(4)	4.874(9)	5.505(7)
C1···O1	5.289(5)	4.645(8)	3.242(6)
C1···O2	3.142(4)	3.401(9)	3.350(6)
C16···O1	4.802(3)	4.839(6)	3.475(6)
C16···O2	3.266(3)	3.369(7)	3.237(6)
ΔvdW/%[b]	–11.5	–5.1	–8.8
M···Ct(N_3)[c]	0.7639(1)	0.6982(3)	0.1042(3)

[a] X = C28 (**10**), C27 (**11**), or C29 (**12**), Y = C30 (**10**) or X (**11**,**12**), Z = C29 (**10**), C28 (**11**), or C30 (**12**). [b] Difference between the C1···O1/2 or C16···O1/2 distance and the sum of the van der Waals radii of O1/2 and the closest terminal methyl group. [c] Displacement of the metal ion from the *N*,*N*,*N* plane of the tripyrrin ligand (doming).

gand. The coordination of the tripyrrin ligand to the voluminous cadmium atom demands a doming of 0.7639(1) Å and an additional distortion of the ligand backbone similar to the *saddling* conformation of the porphyrins.[20] The Cd^{II} ion is bound to the three nitrogen donors at distances of 2.21–2.26 Å. Perpendicular to the TrpyCd subunit the anionic acac^F ligand forms a six-membered chelate ring with an O1–Cd–O2 angle of 80.18(6)° and Cd–O1 and Cd–O2 distances of 2.2873(15) and 2.2613(16) Å, respectively. The CdN_3O_3 core forms a distorted trigonal bipyramidal structure with N2 and O2 in the apices. With respect to the ideal values the angle N1–Cd–N3 of 140.13(6)° shows the largest deviation. Surprisingly, the distance between O2 and the methyl termini C1 and C16 of **29** is found up to 11.5% below the sum of the van der Waals radii, producing a significant amount of intramolecular strain. A six-membered chelate ring thus appears too large for a strainless coordination of two donor centers from one side of a TrpyM subunit.

Single crystals from TrpyCdsal (**11**) were obtained from dichloromethane/*n*-hexane solutions. For **11** one half molecule of dichloromethane per formula unit is present in the crystal lattice. A disorder model with two orientations for the solvent was successfully applied in the solution and refinement of the structure. The results of the crystallographic determination proves the preferential formation of a four-membered over a possible six-membered ring chelate, as observed before in a related nickel(II)-tripyrrin.[10a] The molecular structure of **11** is shown in Figure 8. Table 3 contains selected molecular parameters.

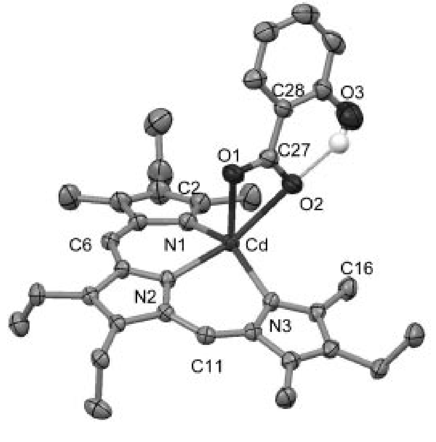


Figure 8. Molecular structure of the salicylato complex TrpyCdsal (**11**) (ellipsoids at 50% probability; CH hydrogen atoms omitted for clarity).

TrpyCdsal can be assigned to a pentacoordinate metallotripyrrin of type **B**. A noticeable feature of the molecular structure of **11** is the severely distorted $C_{14}N_3$ perimeter of the trpyrrin ligand which has a maximum deviation from the mean tripyrrin plane of 0.307(6) Å as compared to only 0.165(3) Å for the related nickel derivative.[10a] The Cd–N bonds of **11** are 2.199(3)–2.221(4) Å long and therefore at the short end of those observed in this series of cadmium complexes. The sal ligand of **11** is coordinated via both carboxylate oxygen atoms to the metal ions with M–O1 being the smaller distance. The aromatic ring of the salicylato ligands and the four-membered CO_2M ring are oriented towards each other in a coplanar fashion, and the sal ligand of **11** is tilted by about 20° from a perpendicular arrangement with the tripyrrin. This finding is caused by an intermolecular π-stacking interaction of the sal group with a C_4N subunit of a neighboring molecule of **11**. The sal complex shows an intramolecular H-bridge from the hydroxy functionality of the salicylato ligands, which binds to O2 with an O2–O3 distance of 2.564(6) Å. This is different from the above-mentioned nickel chelate, where the aryl group is rotated by 180° so as to form a H-bridge with O1. With respect to the O2–C_{term} distance and the *out-of-plane* distortion of the tripyrrin ligand the structure of complex **11** with the four-membered *O*,*O* chelate appears to be more relaxed than that of the six-membered ring chelate TrpyCdacac^F **10**. This finding emphasizes the preference of four- vs. six-membered ring chelate formation on sterically hindered TrpyM fragments.

A different scenario is provided by the structure of the trifluoroacetate **12** (Figure 9, Table 3). The donor strength of the weak OAc^F ligand appears too small to compensate for the strain of a four-membered ring chelate. Therefore, this ring opens at the Cd–O2 bond up to a distance between these atoms of 3.333(3) Å. At the same time, the O2′ donor atom of an adjacent TrpyCdOAc^F molecule coordinates to the free site at the Cd central atom in a distance of 2.346(3) Å. Similar to the NCS/NCSe and the azido/methanol derivatives **7**–**9** a chain structure from coordinatively connected pentacoordinate TrpyCd fragments results. Complex **12** thus escapes the strained situation of a four-membered ring by the formation of a typical coordination polymer with type **A** metallotripyrrin fragments.

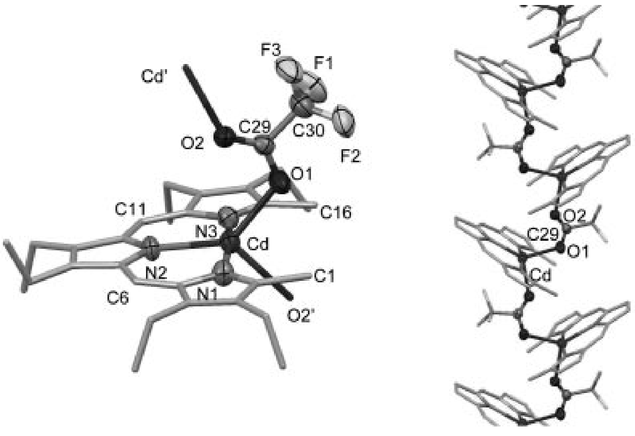


Figure 9. Crystallographically determined structure of the monomeric unit (left; ellipsoids at 50% probability) and the polymeric chain arrangement (right) of TrpyCdOAc^F (**12**) (hydrogen atoms and ethyl groups omitted for clarity).

The trifluoroacetate in **12** functions as a nonsymmetrical bridging ligand. O1 is bound with greater strength to the central metal atom than O2 as indicated by a shorter Cd–O1 bond (Δ = 0.083 Å) and a longer O1–C29 bond (Δ = 0.049 Å). The coordination geometry at the cadmium atom can best be described as distorted trigonal bipyramidal with O1, O2, and N2 at the equatorial and N1, N3 at the apical positions. The distortion is particularly strong at the O1–Cd–O2 angle, which is found to be as narrow as 95.76(11)° instead of the ideal 120°. The monomeric units are organized with a Cd···Cd′ distance of 5.541(2) Å and thus further apart than for the dimeric unit of **9** although the O1···O2 distance is as short as 2.222(3) Å. Other than in the azido case **9** the TrpyCd fragments of **12** are not in a near-coplanar orientation but are found to be bent towards each other by 67.39(17)° and additionally rotated by 172.40(19)°, similar to that found for the pseudohalide species **7** and **8**. The markedly planarized tripyrrin ligand of **12** and the O–C_{term} distances of only 8.8% or less below the sum of the van der Waals radii prove the polymeric form as a largely strain-free assembly and an alternative for cases with weakly bound *O*,*O* chelate ligands. The individual pillars are densely packed in all directions and leave no inner space between the isolated chains. The formation of layers, which was seen in **7**–**9**, is also not detected in this case.

Conclusions

We have shown for a series of pseudohalide and *O*,*O*-chelate ligands that the size of the cadmium(II) ion leads to the formation of tripyrrinatocadmium(II) complexes TrpyCdX with a high propensity for pentacoordination. It appears, that complexes containing the TrpyCd fragment seem to be insufficiently shielded with only four donors at the metal ion and tend to form the desired larger associates. Most of the crystallographically determined molecular structures of these new complexes display coordination polyhedra, which deviate significantly from ideal geometries. The structures are determined by steric factors alone and can be understood on the basis of van der Waals radii and intramolecular interactions. The two limiting geometries **A** and **B** typically obtained for pentacoordinate metallotripyrrins have both also been observed in the case of Cd^{II}.

In all 1D-coordination polymers formed from the TrpyCd fragment the external donor atoms bind from opposite sites of the TrpyCd plane, i.e. in type **A**. Unstrained complexes with almost planar Trpy ligands result from this arrangement. *O*,*O*-Chelating co-ligands, however, usually bind with both oxygen donor atoms from the same side of the TrpyCd unit (type **B**). The presence of two donor atoms in the same segment of the coordination sphere results in additional intramolecular strain. The stresses are compensated for by a shortening of the $O_{donor}\cdots CH_{3term}$ distances and by nonplanar tripyrrin conformations. The weak donor ligand trifluoroacetate in the complex TrpyCdOAc^F (**12**) is not capable of keeping up the strained situation of geometry **B**. In this case a strain-driven polymerization with transformation of the coordination environment to geometry **A** is observed.

To summarize, we have achieved the first general description of the syntheses, spectroscopic properties, and structures of sterically hindered tripyrrinatocadmium(II) complexes.

Experimental Section

General: All reagents were purchased from commercial sources and used as received. Solvents were dried by standard protocols and distilled prior to use. TrpyNiNCO **1** and **2**[10a] and sodium 1,1,1-trifluoroacetylacetonate[21] were prepared according to literature procedures. NMR spectra were obtained with a Bruker AMX 400 spectrometer. Chemical shifts (δ) are given in ppm relative to residual protio solvent resonances (^{1}H spectra), chloroform (^{13}C), or $CFCl_3$ (^{19}F). Mass spectra were recorded with a Finnigan 90 MAT (EI, FAB), Finnigan-MAT 95S (ESI), or the Bruker Biflex IV instrument (MALDI-TOF); *m*/*z* values are given for the most abundant isotopes only. IR spectra were recorded with a Bruker Vector 22 spectrometer in Nujol paste. UV data were collected with a Hitachi U-3200 spectrophotometer. For X-ray crystallographic measurements an IPDS-1 or IPDS-2 instrument from STOE was used.

Preparation of Complexes

Acetato(tripyrrinato)cadmium Complexes 5 and 6 (TrpyCdOAc) from Free Base Tripyrrins. General Procedure: Complexes **1** or **2** of type TrpyNiNCO (0.1 mmol) was dissolved in diethyl ether (40 mL) and treated with a saturated KCN solution (10 mL) at ambient temperature in an ultrasonic bath for 2 h. During this time the color of the mixture changes from green to red. After phase separation the organic layer was washed with water (2 × 20 mL) and dried with sodium sulfate, which resulted in a red ethereal solution of **3** or **4**. These solutions were treated with water (30 mL) and a saturated solution of cadmium(II) acetate in methanol (5 mL). Upon stirring of this mixture for 30 min at ambient temperature the color changes to blue-green. The phases were separated and the organic layer was washed with water (2 × 10 mL) and dried with sodium sulfate. The resulting solution of cadmium complex **5** or **6** can directly be used for further reactions. For **5** an attempt to isolate the compound was performed by reducing the volume of the solution to 5 mL and adding ice-cold pentane. Violet microcrystals of **5** precipitated overnight. Yield: 43.1 mg (77%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.08 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.19 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.87 (s, 3 H, OAc), 2.20 (s, 6 H, 2× CH_3), 2.42 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 2.50 (s, 6 H, 2× CH_3), 2.62 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 6.86 (s, 2 H, 2× H_{meso}) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 10.0, 14.3, 17.4, 17.5, 17.9, 18.2, 21.5, 120.1, 136.0, 139.2, 143.3, 144.6, 145.4, 171.4, 180.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 561 (M^+), 501 ($[M - OAc]^+$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 279 (18000), 350 (69000), 413 (11000), 610 sh (35000), 648 nm (60000 mol^{-1} dm^3 cm^{-1}). IR (Nujol): ν = 1597 ($\nu_{C=C}$), 1553 ($\nu_{C=O}$) cm^{-1}. $C_{28}H_{37}CdN_3O_2$ (560.023): calcd. C 60.05, H 6.66, N 7.50; found C 59.82, H 6.79, N 7.60.

Ligand Exchange by Treatment with Aqueous Salt Solutions. General Procedure: The solution of acetato cadmium complex TrpyCdOAc **5** or **6** (0.1 mmol based on 100% yield) in diethyl ether (30 mL) was treated with a saturated NaY solution (15 mL; Y = anionic ligand) with intense stirring for 16 h. The ether was removed from the mixture in vacuo, and the product was filtered off the aqueous phase and washed with additional water. If the solubility was sufficiently low, the residue was washed with cold pentane or methanol and dried in vacuo.

Thiocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrrinato)cadmium(II) (TrpyCdNCS, 7): Yield: 48.1 mg (86%). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.07 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.15 (t, J = 7.6 Hz, 6 H, 2×CH_2CH_3), 2.19 (s, 6 H, 2× CH_3), 2.43 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 2.56 (s, 6 H, 2× CH_3), 2.65 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 6.92 (s, 2 H, 2× H_{meso}) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 11.3, 16.2, 18.4, 19.3, 19.7, 20.0, 121.7, 138.6, 141.3, 144.6, 146.6, 147.7, 173.4 ppm. MS (70 eV, EI): *m*/*z* (%) = 560 (M^+), 501 ($[M - SCN]^+$). UV/Vis (acetone): λ_{max} (ε) = 345 (58000), 401 (9000), 600 sh (34700), 630 nm (61100 mol^{-1} dm^3 cm^{-1}). IR (Nujol): ν = 2103 (ν_{NCS}), 1595 cm^{-1} ($\nu_{C=C}$). $C_{27}H_{34}CdN_4S$ (559.06): calcd. C 58.01, H 6.13, N 10.02; found C 58.36, H 6.46, N 9.69.

Selenocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrrinato)cadmium(II) (TrpyCdNCSe, 8): Yield: 54.5 mg (90%). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.05 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.16 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 2.19 (s, 6 H, 2× CH_3), 2.42 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 2.55 (s, 6 H, 2× CH_3), 2.66 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 6.94 (s, 2 H, 2× H_{meso}) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 10.2, 15.0, 17.8, 18.2, 18.6, 18.9, 120.6, 134.1, 137.3, 140.2, 145.4, 150.1, 172.1 ppm. MS (70 eV, EI): *m*/*z* (%) = 606 (M^+), 501 ($[M - SeCN]^+$). UV/Vis (acetone): λ_{max} (ε) = 345 (60000), 403 (9000), 595 sh (35000), 631 nm (62000 mol^{-1} dm^3 cm^{-1}). IR (Nujol): ν = 2115 (ν_{NCSe}), 1596 cm^{-1} ($\nu_{C=C}$). $C_{27}H_{34}CdN_4Se$ (605.96): calcd. C 53.51, H 5.66, N 9.25; found C 53.33, H 5.91, N 8.86.

Azido-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrrinato)cadmium(II)·MeOH (TrpyCdN$_3$·MeOH, 9): Purified by recrystallization from methanol/toluene. Yield: 47.1 mg (82%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.09 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.18 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 2.16 (s, 6 H, 2× CH_3), 2.43 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 2.45 (s, 6 H, 2× CH_3), 2.64 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 6.78 (s, 2 H, 2× H_{meso}) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 9.6, 14.4, 15.3, 16.2, 17.3, 17.6, 17.7, 119.1, 136.0, 138.6, 141.5, 143.7, 144.8, 170.8 ppm. MS (70 eV, EI): *m*/*z* (%) = 501 ($[M - MeOH - SeCN]^+$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 (14000), 335 sh (26000), 350 (51000), 413 (10000), 564 sh (14000), 610 sh (24000), 649 nm (41000 mol^{-1} dm^3 cm^{-1}). IR (Nujol): ν = 2090, 2067 (ν_{NNN}), 1594 cm^{-1} ($\nu_{C=C}$). $C_{27}H_{38}CdN_6O$ (575.041): calcd. C 56.39, H 6.66, N 14.61; found C 56.67, H 6.53, N 14.35.

Salicylato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrrinato)cadmium(II) (TrpyCdsal, 10): Yield: 42.1 mg (66%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.05 (t, J = 7.5 Hz, 6 H, 2× CH_2CH_3), 1.20 (t, J = 7.5 Hz, 6 H, 2× CH_2CH_3), 2.19 (s, 6 H, 2× CH_3), 2.39 (q, J = 7.5 Hz, 4 H, 2× CH_2CH_3), 2.51 (s, 6 H, 2× CH_3), 2.62 (q, J = 7.5 Hz, 4 H, 2× CH_2CH_3), 6.88 (s, 2 H, 2× H_{meso}), 6.73–6.78, 6.80–6.82, 7.27–7.33, 7.81–7.83 (4m, 4 H, H_{Ar}), 12.21 (br., 1 H, OH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 10.0, 14.3, 17.4, 17.6, 18.0, 18.2, 116.5, 118.3, 120.0, 131.6, 133.8, 136.1, 139.3, 143.4, 144.5, 145.4, 161.4, 171.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 501 ($[M - sal]^+$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 278 (18000), 350 (69000), 413 (12000), 600 sh (33000), 648 nm (60000 mol^{-1} dm^3 cm^{-1}). IR (Nujol): ν = 3384 (ν_{OH}), 1595 cm^{-1} ($\nu_{C=C}$, $\nu_{C=O}$). $C_{33}H_{39}CdN_3O_3$ (638.092): calcd. C 62.12, H 6.16, N 6.59; found C 61.91, H 6.07, N 6.34.

1,1,1-Trifluoroacetylacetonato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrrinato)cadmium(II) (TrpyCdacac^F, 11): Yield: 39.2 mg (60%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.06 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.20 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.93 (br., 3 H, CH_3 [acac^F]), 2.18 (s, 6 H, 2× CH_3), 2.40 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 2.47 (s, 6 H, 2× CH_3), 2.64 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 5.46 (br., 1 H, CH [acac^F]), 6.86 (s, 2 H, 2× H_{meso}) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 10.0, 14.3, 17.1, 17.3, 18.0, 18.2, 29.8, 120.0, 136.1, 138.9, 143.2, 144.5, 146.0, 172.3 ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2): δ = –76.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 501 ($[M - acac^F]^+$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 276 (18000), 351 (69000), 410 (11000), 605 sh (30000), 652 nm (61000 mol^{-1} dm^3 cm^{-1}). IR (Nujol): ν = 1636, 1612 ($\nu_{C=O}$), 1594 cm^{-1} ($\nu_{C=C}$). $C_{31}H_{38}CdF_3N_3O_2$ (654.059): calcd. C 56.93, H 5.86, N 6.42; found C 56.59, H 5.81, N 6.25.

Trifluoracetato-(3,4,8,9,13,14-hexaethyl-2,15-dimethyltripyrrinato)cadmium(II) (TrpyCdOAc^F, 12): Yield: 43.0 mg (67%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.10 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.19 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 1.20 (t, J = 7.6 Hz, 6 H, 2× CH_2CH_3), 2.42 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 2.51 (s, 6 H, 2× CH_3), 2.62 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 2.63 (q, J = 7.6 Hz, 4 H, 2× CH_2CH_3), 6.87 (s, 2 H, 2× H_{meso}) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 14.8, 17.0, 17.4, 17.8, 17.9, 18.2, 18.4, 120.2, 135.4, 139.5, 144.1, 144.6, 150.2, 171.5 ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2): δ = –74.1 ppm. MS (70 eV, EI): *m*/*z* (%) = 529 ($[M - OAc^F]^+$). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 276 (16000), 350 (65000), 403 (12000), 596 sh (33000), 656 nm (59000 mol^{-1} dm^3 cm^{-1}). IR (Nujol): ν = 1602, 1597 cm^{-1} ($\nu_{C=C}$, $\nu_{C=O}$). $C_{30}H_{38}CdF_3N_3O_2$ (642.048): calcd. C 56.12, H 5.97, N 6.54; found C 55.93, H 6.02, N 6.29.

CCDC-625800 to -625805 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.request/cif.

Supporting Information (see also the footnote on the first page of this article): UV/Vis spectra of **8** in acetone and in MeOH.

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