DOI: 10.1002/ejic.201100072

Synthesis and Structures of Cadmium(II) Complexes with (η^6-Benzenecarboxylate)tricarbonylchromium

Balasubramanian Murugesapandian[a] and Peter W. Roesky*[a]

Dedicated to Professor John D. Corbett on the occasion of his 85th birthday

Keywords: Cadmium / Chromium / Carbonyl ligands / Sandwich complexes / Coordination modes

The reaction of (benzoic acid)tricarbonylchromium [(η^6-C_6H_5COOH)$Cr(CO)_3$] with cadmium acetate in methanol or DMF led to the formation of the dinuclear cadmium compounds [Cd_2{(η^6-C_6H_5COO)$Cr(CO)_3$}$_4$($MeOH)_4$] (**1**) or [Cd_2{(η^6-C_6H_5COO)$Cr(CO)_3$}$_4$($DMF)_4$] (**2**) containing four organometallic ligands with four methanol or DMF molecules coordinated to the cadmium atoms. The reaction of (benzoic acid)tricarbonylchromium [(η^6-C_6H_5COOH)$Cr(CO)_3$] and cadmium acetate with 1,10-phenanthroline (1,10-phen) afforded the dinuclear cadmium complex [Cd_2{(η^6-C_6H_5COO)$Cr(CO)_3$}$_4$(1,10-phen)$_2$] (**3**) with two 1,10-phenanthroline and four organometallic ligands. The reaction of (benzoic acid)tricarbonylchromium [(η^6-C_6H_5COOH)$Cr(CO)_3$] with cadmium acetate in the presence of 4,4′-bipyridine (4,4′-bipy) led to the one-dimensional coordination polymer [Cd_2{(η^6-C_6H_5COO)$Cr(CO)_3$}$_4$(4,4′-bipy)$_2$·3DMF]$_n$ (**4**) containing a dinuclear cadmium complex as a repeating unit. The solid-state structures of all the compounds were determined by single-crystal X-ray diffraction.

Introduction

Arene complexes of the type [(η^6-arene)$M(CO)_3$] (M = Cr, Mo, W)[1–3] are well established in organic synthesis.[4] The derivative (benzoic acid)tricarbonylchromium was first reported in 1958 by Fischer et al.[5,6] Although these compounds have been known for a long time, the number of structurally characterized derivatives is very limited. To the best of our knowledge, besides [(η^6-C_6H_5COOH)$Cr(CO)_3$] and [{η^6-*p*-$C_6H_4(COOH)_2$}$Cr(CO)_3$][7–9] and some related group 6 compounds,[9,10] only the group 4 metal benzenecarboxylate complexes [(η^5-$C_5H_5)_2$TiX{(μ-$O_2CC_6H_5$)$Cr(CO)_3$}] (X = Cl, Br, CH_3) and [(η^5-$C_5H_5)_2$M{(μ-$O_2CC_6H_5$)$Cr(CO)_3$}$_2$] (M = Ti, Zr)[11] had been structurally characterized before we started our investigation last year (see below).[12,13] Recently, (benzoic acid)tricarbonylchromium and its derivatives have been used as building blocks for the construction of polymeric materials. It was shown in 1990 that (benzoic acid)tricarbonylchromium and its derivatives form extended arrays in which the molecules are linked by hydrogen bonds.[7,8] Moreover, [(η^6-arene)tricarbonylchromium] complexes have been used to form bimetallic complexes,[14,15] mesomorphic materials,[16] polymers,[17,18] macrocycles,[19] and receptors.[20] Recently, Kaye and Long reported the synthesis of [Zn_4O{(1,4-benzenedicarboxylate)$Cr(CO)_3$}], which is a porous metal–organic framework.[21] Under photolytic conditions, substitution of a single CO ligand per metal by N_2 and H_2 was observed. This kind of reactivity has also been observed in discrete complexes.[22] Theoretical studies have shown that the stability and reactivity of $Cr(CO)_3$ species can be modulated by grafting them to metal–organic frameworks (MOFs) with different organic linkers. These studies have shown that electron acceptors such as $C_6H_4(COOH)_2$-substituted MOF linkers facilitate the substitution of CO by incoming molecules.[23] Very recently, Egbert and Heinekey reported the synthesis and characterization of [(η^6-arene)$M(CO)_2(H_2)$][24] (M = Cr, Mo, W). The incorporation of metallo ligands into coordination polymers is still rare.[25–33] In this context we became interested in using (benzoic acid)tricarbonylchromium as a starting material[5,6] for the construction of oligomeric and polymeric materials. Our intention was to study the influence of the organometallic compound on the formation process and on the structures of the coordination compounds in a systematic way. Further derivatization of the tricarbonylchromium unit by classic thermal or photolytic activation methods seemed to be possible. Because (arene)tricarbonylchromium complexes are known to be relatively robust, we started our investigations with this class of compounds. Recently we published the synthesis and structural characterization of the sodium and potassium salts of (η^6-benzenecarboxylate)tricarbonylchromium and (η^6-1,4-benzenedicarboxylate)tricarbonylchromium.[12] These com-

[a] Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT),
Engesserstr. 15, 76128 Karlsruhe, Germany
Fax: +49-721-6084-4854
E-mail: roesky@kit.edu

pounds form one- and two-dimensional networks in the solid state. Moreover, we have reported the zinc coordination polymers based on (η^6-benzenecarboxylate)tricarbonylchromium.[13] In contrast to the coordination chemistry of ferrocenyl-substituted carboxylic acid,[34–39] to the best of our knowledge no cadmium complexes have been published with (η^6-benzenecarboxylate)tricarbonylchromium as metallo ligands.

The coordination chemistry of cadmium in both biological and nonbiological fields has attracted research interest.[40] The spherical d^{10} configuration of Cd^{II} enables a flexible coordination environment of the metal center, which forms coordination numbers of four, five, and six. Some examples are also known with a coordination number of seven.

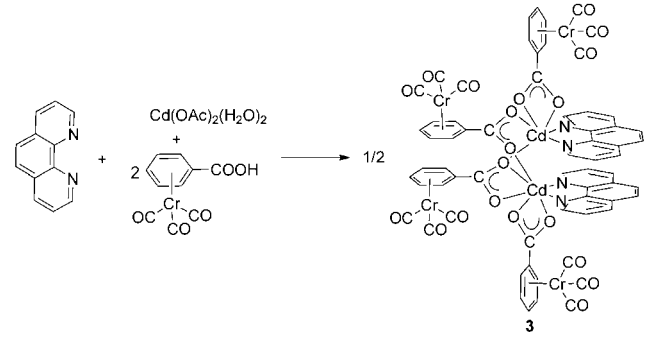
Herein we report the coordination chemistry of (η^6-benzenecarboxylic acid)tricarbonylchromium as organometallic ligands of cadmium metal ions. The reaction was investigated with and without nitrogen-containing ancillary ligands. Depending upon the ancillary ligand either dinuclear compounds or one-dimensional coordination polymers were formed.

Results and Discussion

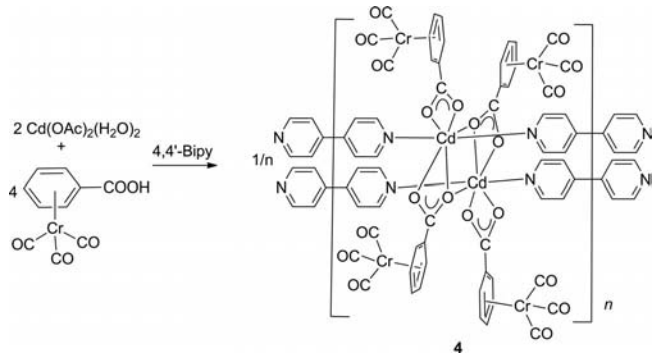
The reaction of (benzoic acid)tricarbonylchromium with cadmium acetate in methanol or DMF afforded the novel dinuclear complexes $[Cd_2\{(\eta^6\text{-}C_6H_5COO)Cr(CO)_3\}_4(MeOH)_4]$ (**1**) or $[Cd_2\{(\eta^6\text{-}C_6H_5COO)Cr(CO)_3\}_4(DMF)_4]$ (**2**) in good yields (Scheme 1). Treatment of 1,10-phenanthroline with (benzoic acid)tricarbonylchromium and cadmium acetate in a methanol/DMF mixture gave the dinuclear complex $[Cd_2\{(\eta^6\text{-}C_6H_5COO)Cr(CO)_3\}_4(1,10\text{-phen})_2]$ (**3**; Scheme 2), whereas the reaction of 4,4′-bipyridine with (benzoic acid)tricarbonylchromium and cadmium acetate led to the one-dimensional coordination polymer $[Cd_2\{(\eta^6\text{-}C_6H_5COO)Cr(CO)_3\}_4(4,4'\text{-bipy})_2\cdot 3DMF]_n$ (**4**; Scheme 3). All new compounds were characterized by standard analytical/spectroscopic techniques and the solid-state structures were determined by single-crystal X-ray diffraction.

The ^1H NMR spectra of compounds **1**–**4** show three signals for the (benzenecarboxylate)tricarbonylchromium unit in the range δ = 6.30–5.82 ppm. Signals from coordinated solvent molecules are seen for compounds **1** (methanol: δ = 4.09 and 3.17 ppm) and **2** (DMF: δ = 7.95, 2.89 and 2.73 ppm). In compound **3**, resonances of the ancillary ligand 1,10-phenanthroline were detected at δ = 9.17, 8.78, 8.17, and 7.97 ppm. The signals of the ancillary ligand 4,4′-bipyridine in compound **4** were observed as broad signals at δ = 8.73 and 7.85 ppm. The $^{13}C\{^1H\}$ NMR spectra of all compounds show the expected sets of signals. Characteristic signals of the carbonyl groups were observed at $\delta \approx$ 233.4 ppm and signals of the carboxylate groups were observed at $\delta \approx$ 169.0 ppm. In the IR spectra the A_1 and E νCO stretching frequencies were measured at 1959 and 1868 cm^{-1} (**1**), 1961 and 1877 cm^{-1} (**3**), and 1959 and 1871 cm^{-1} (**4**). Compound **2** shows broad signals around 1853 cm^{-1} for the carbonyl group.

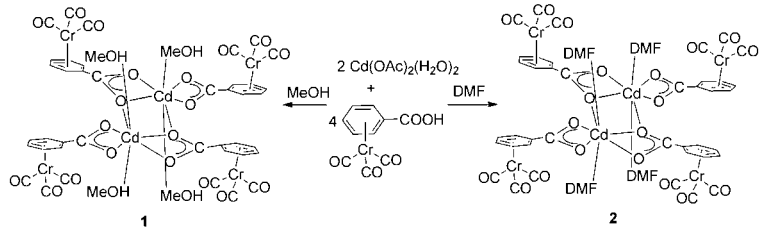
Crystals of compounds **1**–**4** were grown in the dark because of the light sensitivity of the reaction mixture. When exposed to daylight they decompose and change color. Compound **1** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure of compound **1** contains four $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ carboxylate anions, two cadmium atoms, and four methanol molecules (Figure 1). In



Scheme 2.



Scheme 3.



Scheme 1.

compound **1** the carboxylate anions coordinate in two different modes. One coordination mode is bidentate chelating and the other is a tridentate metal-bridging coordination mode. Of the four carboxylate anions, two carboxylate anions (Cr2 and Cr2′) bridge the two cadmium atoms Cd1 and Cd1′ and the other two act as a chelating ligand towards the two different cadmium atoms. The cadmium atom, which is seven-fold coordinated, is in the center of a distorted pentagonal bipyramidal coordination environment with five oxygen atoms from three different carboxylate anions comprising the equatorial plane, with two coordinated methanol molecules occupying the axial positions.

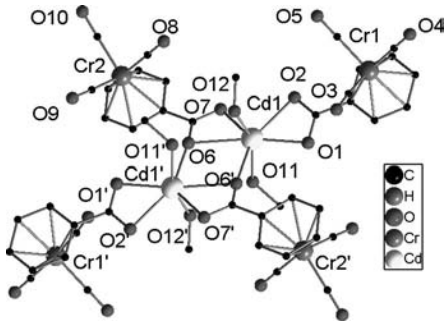


Figure 1. Molecular structure of compound **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cd1–O1 2.3190(2), Cd1–O2 2.3937(2), Cd1–O(6) 2.3024(2), Cd1′–O6 2.565(2), Cd1′–O7 2.2924(2), Cd1′-O11 2.3411(2), Cd1–O12 2.295(2), O7′–Cd1–O12 97.62(9), O7′–Cd1–O6 128.99(7), O12–Cd1–O6 78.01(9), O7′–Cd1–O1 138.44(6), O12–Cd1–O1 95.09(8), O6–Cd1–O1 92.33(7), O7′–Cd1–O11 85.03(7), O12–Cd1–O11 156.42(8), O(6)–Cd(1)–O(11) 82.14(7), O1–Cd1–O11 98.33(7), O7′–Cd1–O2 84.38(6), O12–Cd1–O2 92.82(8), O6–Cd1–O2 146.01(6), O1–Cd1–O2 55.54(6), O11–Cd1–O2 110.77(6), O7′–Cd1–O6′ 53.41(6), O12–Cd1–O6′ 80.64(8), O6–Cd1–O6′ 75.97(6).

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of compound **2** is similar to compound **1**, except that the four methanol molecules are replaced by four DMF molecules (Figure 2). The asymmetric unit consists of one cadmium atom, two carboxylate anions (Cr1 and Cr2), and two coordinated disordered DMF molecules. Thus, the cadmium atom, which is seven-fold coordinated, is in the center of a distorted pentagonal bipyramidal coordination polyhedron. The metal atom is surrounded by five oxygen atoms from three different carboxylate anions comprising the equatorial plane with two coordinated DMF molecules located in the axial positions.

The addition of nitrogen-containing ancillary ligands has a significant influence on the structure. By using 1,10-phenanthroline as a chelating nitrogen-containing ancillary ligand a coordination compound with a different structure was observed. The 1,10-phenanthroline-containing compound **3** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two cadmium atoms, two 1,10-phenanthroline ligands, and four carboxylate {η^6-C_6H_5COO}$Cr(CO)_3$ anions (Figure 3). The cadmium atom is in a seven-fold coordination environment with five oxygen atoms from three {η^6-C_6H_5COO}$Cr(CO)_3$ carboxylate

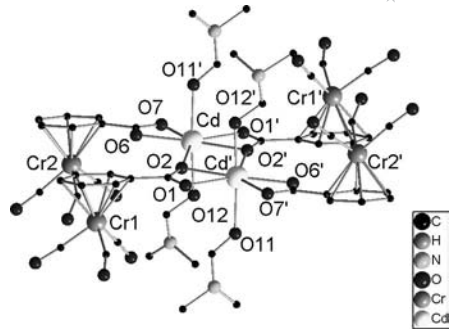


Figure 2. Molecular structure of compound **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cd–O1 2.345(9), Cd–O2 2.409(7), Cd′–O2 2.448(8), Cd–O6 2.268(9), Cd–O7 2.563(7), Cd–O11 2.339(10), Cd–O12 2.312(9), O6–Cd–O12 95.4(3), O6–Cd–O11 86.9(4), O12–Cd–O11 173.5(4), O6–Cd–O1 143.1(3), O12–Cd–O1 86.7(3), O11–Cd–O1 87.7(4), O6–Cd–O2 88.5(3), O12–Cd–O2 84.5(3), O11–Cd–O2 101.7(3), O1–Cd–O2 128.3(3), O6–Cd–O2′ 162.0(3), O12–Cd–O2′ 88.8(3), O11–Cd–O2′ 90.9(3), O1–Cd–O2′ 54.4(3), O2–Cd–O2′ 74.5(3), O6–Cd–O7 53.7(3), O12–Cd–O7 87.7(3), O11–Cd–O7 88.8(3), O1–Cd–O7 89.8(3), O2–Cd–O7 140.4(3), O2′–Cd–O7 144.2(3).

anions and two nitrogen atoms from 1,10-phenanthroline forming a distorted mono-capped trigonal prism (Figure 4). Two cadmium atoms are connected by two bridging {η^6-C_6H_5COO}$Cr(CO)_3$ carboxylate anions to form a dinuclear species. The {η^6-C_6H_5COO}$Cr(CO)_3$ carboxylate anions are involved in two different kinds of coordination modes. One is a bidentate chelating coordination mode and the other is a tridentate bridging coordination mode. The Cd–O bond lengths of the carboxylate groups reveal the difference between the monodentate and bridging coordination mode. The Cd–O bond lengths of the bridging carboxylate groups are Cd1–O6 2.317(3), Cd2–O6 2.728(3), Cd2–O12 2.313(3), and Cd1–O12 2.8764 Å. The chelating carboxylate groups form Cd–O bonds with lengths in the range of 2.248(3) to 2.497(3) Å. The Cd–N bond lengths are in the range of 2.314(3) to 2.362(3) Å. The molecular structure of compound **3** is similar to the molecular structure of a compound obtained from 2-hydroxybenzoic acid, 1,10-phenanthroline, and cadmium acetate.[41] Changing the carboxylic acid from 2-hydroxybenzoic acid to chloropropionic acid gave a dicadmium species with a different structure. The structure contains four carboxylate groups, two 1,10-phenanthroline ligands, and two cadmium atoms.[42] On the other hand, the reaction of 1,10-phenanthroline and cadmium acetate with sodium *p*-ferrocenylbenzoate yielded a mononuclear complex containing one 1,10-phenanthroline, two carboxylate groups, and one water molecule.[35]

With 4,4′-bipyridine as a nitrogen-containing ancillary ligand a one-dimensional coordination polymer was obtained. Compound **4** crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit of this molecule contains one cadmium atom, two {η^6-C_6H_5COO}$Cr(CO)_3$ carboxylate anions, two half 4,4′-bipyridine ligands, and one and half noncoordinated DMF molecules. Compound **4** forms a one-dimensional coordination polymer consisting of a dinuclear cadmium subunit, which is coordinated by four {η^6-

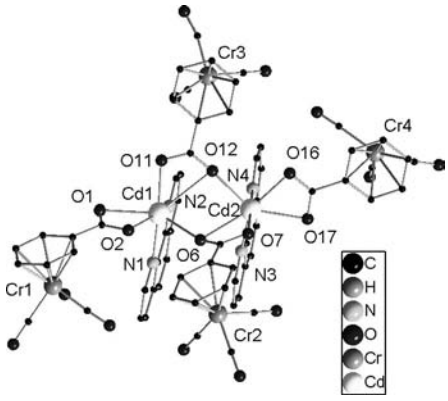


Figure 3. Molecular structure of compound **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cd1–N1 2.362(3), Cd1–N2 2.322(4), Cd2–N3 2.354(3), Cd2–N4 2.314(3), Cd1–O1 2.497(3), Cd1–O2 2.304(4), Cd1–O6 2.317(3), Cd2–O7 2.248(3), Cd1–O11 2.267(3), Cd2–O12 2.313(3), Cd2–O16 2.320(3), Cd2–O17 2.437(3), Cd2–O6 2.729(3), Cd1–O12 2.879(3), O11–Cd1–O2 99.60(12), O11–Cd1–O6 109.96(13), O2–Cd1–O6 86.26(12), O11–Cd1–N2 94.14(13), O2–Cd1–N2 153.35(11), O6–Cd1–N2 110.37(11), O11–Cd1–N1 163.81(14), O2–Cd1–N1 91.85(13), O6–Cd1–N1 82.02(12), N2–Cd1–N1 70.98(13), O11–Cd1–O1 89.41(12), O2–Cd1–O1 54.67(11), O6–Cd1–O1 139.35(11), N2–Cd1–O1 103.13(11), N1–Cd1–O1 87.91(12), O7–Cd2–O12 98.37(13), O7–Cd2–N4 175.12(11), O12–Cd2–N4 84.23(12), O7–Cd2–O16 95.07(12), O12–Cd2–O16 90.29(13), N4–Cd2–O16 89.03(12), O7–Cd2–N3 103.90(12), O12–Cd2–N3 119.48(13), N4–Cd2–N3 71.22(12), O16–Cd2–N3 141.02(11), O7–Cd2–O17 93.70(12), O12–Cd2–O17 144.62(12), N4–Cd2–O17 86.44(12), O16–Cd2–O17 55.46(10), N3–Cd2–O17 89.17(11).

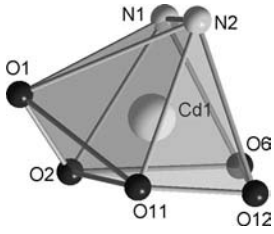


Figure 4. Coordination environment around the cadmium atom (Cd1) in compound **3**.

$C_6H_5COO\}Cr(CO)_3$ anions (Figure 5). These subunits are bridged by two 4,4′-bipyridine linkers. The cadmium atom is seven-fold coordinated. The coordination geometry is best described as a distorted pentagonal bipyramid. The cadmium atom is surrounded by five oxygen atoms in the equatorial positions from three $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ carboxylate anions with two nitrogen atoms in the axial positions from 4,4′-bipyridine ligands. The structure of this compound is somewhat similar to compounds **1** and **2**. Formally, methanol (**1**) and DMF (**2**) molecules are replaced by coordinating 4,4′-bipyridine ligands.

Thermogravimetric analysis (TGA) was performed on the polymeric compound **4**. Compound **4** is thermally relative robust as shown by the TGA (Figure 6). The TGA curve of compound **4** shows the loss of three molecules of DMF in the temperature range of 90–148 °C (obsd. 11.8%; calcd. 12.3%). Then the compound slowly decomposes up

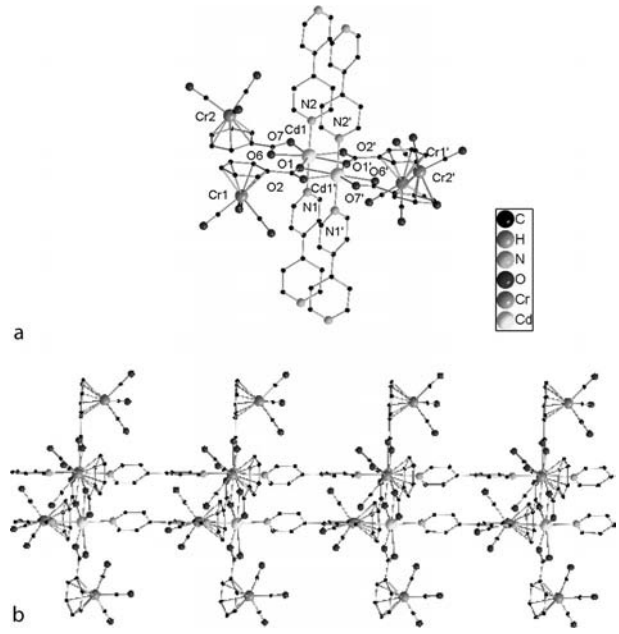


Figure 5. Molecular structure of compound **4**. Hydrogen atoms have been omitted for clarity. Top: Two units of the polymeric chain. Bottom: Cut-out of the polymeric structure. Selected bond lengths [Å] and angles [°]: Cd1–N1 2.314(5), Cd1–N2 2.321(5), Cd1–O1 2.395(6), Cd1′–O1 2.518(6), Cd1–O2 2.361(6), Cd1–O6 2.326(6), Cd1–O7 2.451(6), N1–Cd–N2 174.9(2), N2–Cd1–O6 95.0(2), N1–Cd1–O6 87.2(2), N2–Cd1–O2 91.3(2), N1–Cd1–O2 89.7(2), O6–Cd1–O2 143.0(2), N2–Cd1–O1 87.4(2), N1–Cd1–O1 88.2(2), O6–Cd1–O1 85.4(2), O2–Cd1–O1 131.37(2), N2–Cd1–O7 91.2(2), N1–Cd1–O7 93.9(2), O6–Cd1–O7 54.7(2), O2–Cd1–O7 88.87(2) O1–Cd1–O7 139.74(2), N2–Cd1–O1′ 88.4(2), N1–Cd1–O1′ 88.1(2), O6–Cd1–O1′ 162.9(2), O2–Cd1–O1′ 53.37(2), O1–Cd1–O1′ 78.0(2), O7–Cd1–O1′ 142.21(2).

to 402 °C. The weight loss corresponds to the loss of 12 CO molecules and the organic units. The weight loss of this step is 51%.

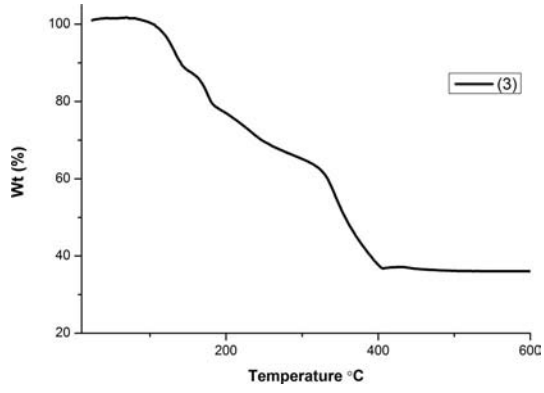


Figure 6. TGA curves for **4** in the temperature range 25–600 °C at a heating rate of 5 °C/min under N_2.

Conclusions

Three dinuclear complexes and one coordination polymer of cadmium with organometallic ligand $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ have been obtained by the reaction of

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[(η^6-C_6H_5COOH)Cr(CO)$_3$] with cadmium acetate in the presence or absence of ancillary ligands. In the absence of an ancillary ligand or in the presence of the chelating ancillary ligand 1,10-phenanthroline dinuclear complexes were obtained. By using 4,4′-bipyridine as an ancillary ligand the formation of a one-dimensional coordination polymer was observed. The {η^6-C_6H_5COO}Cr(CO)$_3$ carboxylate anion is coordinated in two different coordination modes. One is a bidentate chelating coordination mode whereas the other is a tridentate bridging coordination mode. In all the reported compounds the cadmium atoms are seven-fold coordinated.

Experimental Section

General: Deuteriated solvents were obtained from Aldrich (99 atom-% D). NMR spectra were recorded with a Bruker Avance II 300 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained with a Bruker FTIR Tensor 37 spectrometer using the attenuated total reflection method (ATR). Elemental analyses were carried out with an Elementar Vario EL instrument. TGA was carried out with a Netzsch STA 429 instrument. The solvents were used as purchased from commercial sources without further purification. [(η^6-C_6H_5COOH)Cr(CO)$_3$] was prepared according to literature procedures.[7,8]

[Cd$_2${(η^6-C_6H_5COO)Cr(CO)$_3$}$_4$(MeOH)$_4$] (1): Cadmium acetate (54.0 mg, 0.200 mmol) was added to a solution of [(η^6-C_6H_5COOH)Cr(CO)$_3$] (101 mg, 0.400 mmol) in methanol (10 mL) and the subsequent solution was stirred for 6 h. While stirring a yellow precipitate was formed, which was dissolved by heating. The hot solution obtained was then filtered and kept for crystallization; yield 200 mg (71% based on Cd). ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): δ = 6.30 (d, 8 H, Ar), 5.88 (t, 4 H, Ar), 5.66 (t, 8 H, Ar), 4.09 (q, 4 H, OH), 3.17 (d, 12 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]-DMSO, 75 MHz, 25 °C): δ = 233.4, 169.0, 99.6, 97.9, 97.2, 92.6, 48.6 ppm. IR: $\tilde{\nu}$ = 3095 (br), 2500 (br), 2159 (s), 2026 (sh), 1959 (s), 1868 (s), 1593 (sh), 1557 (s), 1527 (s), 1499 (sh), 1397 (s), 1177 (sh), 1149 (s), 1069 (s), 1027 (sh), 1088 (s), 960 (sh), 944 (sh), 886 (s), 855 (s), 828 (s), 785 (s), 720 (s), 684 (s), 657 (s), 623 (s), 531 (s) cm^{-1}. $C_{44}H_{36}Cd_2Cr_4O_{24}$ (1381.54): C 38.25, H 2.63; found C 36.69, H 2.65.

[Cd$_2${(η^6-C_6H_5COO)Cr(CO)$_3$}$_4$(DMF)$_4$] (2): [(η^6-C_6H_5COOH)Cr-(CO)$_3$] (101 mg, 0.400 mmol) was dissolved in DMF (5 mL). Cadmium acetate (54.0 mg, 0.200 mmol) was added to this solution and the subsequent solution was stirred for 6 h. While stirring a yellow precipitate was formed, which was dissolved by heating. The solution obtained was kept for crystallization; yield 210 mg (67% based on Cd). ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): δ = 7.95 (s, 4 H, CH), 6.30 (d, J = 6 Hz, 8 H, Ar), 5.89 (t, J = 6 Hz, 4 H, Ar), 5.66 (t, 8 H, Ar), 2.89 (s, 12 H, CH$_3$), 2.73 (s, 12 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 75 MHz, 25 °C): δ = 233.4, 169.0, 162.3, 99.6, 97.9, 97.3, 92.6, 35.8, 30.8 ppm. IR: $\tilde{\nu}$ = 3096 (br), 2930 (br), 1853 (br), 1571 (s), 1552 (sh), 1525 (s), 1496 (sh), 1455 (s), 1433 (sh), 1379 (s), 1249 (sh), 1150 (s), 1103 (s), 1054 (s), 1013 (sh), 962 (s), 944 (s), 891 (s), 848 (s), 826 (sh), 783 (s), 681 (sh), 661 (sh), 623 (s), 533 (s) cm^{-1}. $C_{52}H_{48}Cd_2Cr_4N_4O_{24}$ (1545.75): calcd. C 40.41, H 3.13, N 3.62; found C 40.43, H 3.07, N 3.59.

[Cd$_2${(η^6-C_6H_5COO)Cr(CO)$_3$}$_4$(1,10-phen)$_2$] (3): 1,10-Phenanthroline (36.0 mg, 0.200 mmol) and cadmium acetate (54.0 mg, 0.200 mmol) were dissolved in methanol (10 mL) and the subsequent solution was stirred for 1 h. [(η^6-C_6H_5COOH)Cr(CO)$_3$] (101 mg, 0.400 mmol) was added to this solution, which was stirred for 6 h. While stirring a yellow precipitate formed. Slow evaporation of the methanol/DMF mixture gave yellow crystals; yield 230 mg (70% based on Cd). ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): δ = 9.17 (br., 4 H, Phen), 8.78 (d, 4 H, Phen), 8.17 (s, 4 H, Phen), 7.97 (m, 4 H, Phen), 6.25 (d, J = 6 Hz, 8 H, Ar), 5.82 (t, J = 6 Hz, 4 H, Ar), 5.62 (t, J = 6 Hz, 8 H, Ar) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 75 MHz, 25 °C): δ = 233.4, 169.0, 150.1, 140.1, 139.2, 128.7, 127.0, 125.1, 99.8, 97.6, 96.9, 93.0 ppm. IR: $\tilde{\nu}$ = 3087 (br), 2505 (br), 1961 (s), 1877 (s), 1670 (s), 1568 (s), 1520 (sh), 1550 (sh), 1449 (sh), 1424 (sh), 1389 (s), 1147 (s), 1099 (s), 1045 (s), 1014 (s), 992 (s), 953 (s), 847 (s), 826 (s), 785 (sh), 724 (s), 684 (s), 657 (s), 625 (s), 536 (s) cm^{-1}. $C_{64}H_{36}Cd_2Cr_4N_4O_{20}$ (1613.79): calcd. C 47.63, H 2.25, N 3.47; found C 47.74, H 2.29, N 3.48.

[Cd$_2${(η^6-C_6H_5COO)Cr(CO)$_3$}$_4$(4,4′-bipy)$_2$·3DMF]$_n$ (4): [(η^6-C_6H_5COOH)Cr(CO)$_3$] (101 mg, 0.400 mmol) was dissolved in DMF (10 mL). Cadmium acetate (54.0 mg, 0.200 mmol) was added to this solution. After stirring for 1 h, 4,4′-bipyridine (32.0 mg, 0.200 mmol) was added and the subsequent solution was stirred for 6 h. While stirring a yellow precipitate formed, which was dissolved by heating. The solution obtained was kept for crystallization; yield 215 mg (59% based on Cd). ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): δ = 8.73 (br., 8 H, Ar), 7.95 (s, 3 H, CH), 7.85 (br., 8 H, Ar), 6.30 (d, J = 6 Hz, 8 H, Ar), 5.87 (t, J = 6 Hz, 4 H, Ar), 5.65 (t, J = 6 Hz, 8 H, Ar), 2.87 (s, 9 H, CH$_3$), 2.71 (s, 9 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 75 MHz, 25 °C): δ = 233.3, 169.2, 162.3, 150.9, 144.5, 127.8, 121.5, 97.9, 97.2, 92.3, 35.8, 30.8 ppm. IR: $\tilde{\nu}$ = 3091 (br), 2934 (br), 1959 (s), 1871 (s), 1670 (s), 1597 (sh), 1565 (s), 1542 (sh), 1499 (sh), 1389 (s), 1255 (sh), 1221 (s), 1174 (sh), 1147 (s), 1093 (s), 1069 (s), 1009 (sh), 941 (s), 850 (s), 811 (s), 789 (s), 720 (sh), 683 (s), 658 (s), 627 (s), 572 (sh), 533 (s) cm^{-1}. $C_{69}H_{57}Cd_2Cr_4N_7O_{23}$ (1785.03): calcd. C 46.43, H 3.20, N 5.49; found C 47.39, H 3.24, N 5.53.

X-Ray Crystallographic Studies of 1–4: A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2T diffractometer at –73 °C.

All structures were solved by the Patterson method (SHELXS-97[43]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, for which the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes determined by using the program SHELXL-97.[43] The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

CCDC-808699 (for **1**), -808700 (for **2**), -808701 (for **3**), and -808702 (for **4**) 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.

Crystal Data for 1: $C_{44}H_{36}Cd_2Cr_4O_{24}$, M = 1381.53, monoclinic, a = 7.9638(16), b = 10.725(2), c = 30.465(6) Å, β = 93.45(3)°, V = 2597.5(9) Å^3, T = 200(2) K, space group $P2_1/c$, Z = 2, μ(Mo-K_α) = 1.693 mm^{-1}, 48455 reflections measured, 7009 independent reflections (R_{int} = 0.0508), 5897 observed reflections. The final R_1 values were 0.0304 [$I > 2\sigma(I)$]. The final $wR(F^2)$ values were 0.0826 (all data).

Crystal Data for 2: $C_{52}H_{48}Cd_2Cr_4N_4O_{24}$, M = 1545.74, triclinic, a = 10.509(2), b = 10.688(2), c = 13.884(3) Å, α = 78.14(3), β = 75.69(3), γ = 74.84(3)°, V = 1441.9(5) Å^3, T = 200(2) K, space group $P\bar{1}$, Z = 1, μ(Mo-K_α) = 1.537 mm^{-1}, 26998 reflections measured, 7745 independent reflections (R_{int} = 0.2083), 4273 observed reflections. The final R_1 values were 0.1095 [$I > 2\sigma(I)$]. The final $wR(F^2)$ values were 0.3244 (all data).

Crystal Data for 3: $C_{64}H_{36}Cd_2Cr_4N_4O_{20}$, M = 1613.77, triclinic, a = 13.770(3), b = 15.041(3), c = 15.791(3) Å, α = 88.90(3), β = 70.57(3), γ = 78.64(3)°, V = 3020.1(11) Å^3, T = 200(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-K_α) = 1.468 mm^{-1}, 33220 reflections measured, 16135 independent reflections (R_{int} = 0.0509), 10632 observed reflections. The final R_1 values were 0.0495 [$I > 2\sigma(I)$]. The final $wR(F^2)$ values were 0.1247 (all data).

Crystal Data for 4: $C_{69}H_{57}Cd_2Cr_4N_7O_{23}$, M = 1785.02, monoclinic, a = 34.351(7), b = 11.694(2), c = 20.142(4) Å, β = 113.03(3)°, V = 7447(3) Å^3, T = 150(2) K, space group $C2/c$, Z = 4, μ(Mo-K_α) = 1.203 mm^{-1}, 32355 reflections measured, 7322 independent reflections (R_{int} = 0.1710), 4397 observed reflections. The final R_1 values were 0.0734 [$I > 2\sigma(I)$]. The final $wR(F^2)$ values were 0.2147 (all data).

Acknowledgments

This work was supported by the Alexander-von-Humboldt Stiftung (fellowship to B.M.), the DFG Center for Functional Nanostructures (CFN), and the Landesstiftung Baden-Württemberg GmbH.

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Received: January 20, 2011
Published Online: April 14, 2011

