1698 *Inorg. Chem.* **2011**, *50*, 1698–1704
DOI: 10.1021/ic102167t

Inorganic Chemistry
Article

Coordination Polymers of Zinc with (η^6-Benzenecarboxylate) Chromium Tricarbonyl

Balasubramanian Murugesapandian and Peter W. Roesky*

Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstrasse 15,
76131 Karlsruhe, Germany

Received October 28, 2010

Different coordination polymers were obtained by the reaction of (benzoic acid) chromium tricarbonyl with zinc acetate in the presence of various organic dipyridyl linkers. Depending on the nature of the linker either monomeric or polymeric compounds were obtained. Reactions of (benzoic acid) chromium tricarbonyl with zinc acetate and bidentate pyridine based ligands 4,4′-bipyridine (4,4′-bipy), 1,2-bis(4-pyridyl)ethane (bpe), 1,3-bis(4-pyridyl)propane (tmdp), and 2,2′dipyridylamine (DPA) afforded the novel coordination polymers $[\mathrm{Zn}[\{\eta^6\text{-}\mathrm{C_6H_5COO}\}\mathrm{Cr(CO)_3}]_2(4,4'\text{-bipy})]_n$, $[\mathrm{Zn}[\{\eta^6\text{-}\mathrm{C_6H_5COO}\}\mathrm{Cr(CO)_3}]_2(\mathrm{bpe})]_n$, $[\mathrm{Zn}[\{\eta^6\text{-}\mathrm{C_6H_5COO}\}\mathrm{Cr(CO)_3}]_2(\mathrm{tmdp})\}]_n$, and the monomeric complex $[\mathrm{Zn}[\{\eta^6\text{-}\mathrm{C_6H_5COO}\}\text{-}\mathrm{Cr(CO)_3}]_2(\mathrm{DPA})]$. The solid state structures of all compounds were determined by single crystal X-ray diffraction. By using 1,3-bis(4-pyridyl)propane as a linker a chiral infinite helical structure was formed in the solid state. Thermogravimetric analysis (TGA) studies showed that upon heating the carbonyl groups of the $\{\eta^6\text{-}\mathrm{C_6H_5COO}\}\mathrm{Cr(CO)_3}$ anion were lost before the organic ligand sphere was thermally decomposed.

Introduction

During the past decade, metal−organic frameworks (MOFs) and infinite coordination polymers (ICPs) have been studied extensively.[1−7] These polymeric frameworks show an enormous variety of interesting molecular-based topologies, the potential variety of properties, and promising applications such as in gas storage,[8] catalysis,[9] and sensors for special classes of molecules.[10,11] Some of these materials also show excellent magnetic[12] and luminescent properties,[13,14] and interesting optoelectronic effects.[15] As summarized recently Zn^{2+} as a d^{10} metal ion is particularly suitable for the construction of coordination polymers and networks.[6,16−20] The spherical d^{10} configuration enables a flexible coordination environment of the metal center. Different coordination geometries of zinc complexes such as tetrahedral, trigonal bipyramidal, square pyramidal, and octahedral have been observed.[17] As a result of the lability of zinc coordination compounds rearrangements of the ligands may occur during the formation of the coordination polymers resulting in highly ordered network structures. There are also reports on coordination polymers that exhibit infinite double-helical motifs in the solid state. Incorporation of metallo ligands into the coordination polymers is still rare.[19,21−28] Most of the used compounds are based on ferrocene as metallo ligand.[19,21,27,28] Recently, we became

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*To whom correspondence should be addressed. E-mail: roesky@kit.edu.

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interested in coordination polymers based on (benzenecarboxylate) chromium tricarbonyl. Already in 1990 it was reported that (benzoic acid) chromium tricarbonyl and its derivatives formed extended arrays in which the molecules are linked by hydrogen bonds.[29,30] Moreover, [(η^6-arene) chromium tricarbonyl] complexes are used to form bimetallic complexes,[31,32] mesomorphic materials,[33] polymers,[34,35] and macrocycles.[36] Lately, Long and co-workers reported on the synthesis of $[Zn_4O\{(1,4\text{-benzenedicarboxylate})Cr(CO)_3]$, which is a porous MOF.[37] Under photolysis conditions substitution of a single CO ligand per metal by N_2 or H_2 was observed. Similar results were obtained for the discrete complexes.[38] Theoretical studies have modulated the stability and the reactivity of $Cr(CO)_3$ species by grafting them to MOFs with different organic linkers. These studies have shown that electron-acceptors such as $C_6H_4(COOH)_2$ substituted MOF linkers facilitated the substitution of CO by incoming molecules.[39] Whereas Long and co-workers reacted the microporous MOF $[Zn_4O(1,4\text{-benzenedicarboxylate})_3]$ with $Cr(CO)_6$ to form the functionalized MOF $[Zn_4O\{(1,4\text{-benzenedicarboxylate})\text{-}Cr(CO)_3\}_3]$, we were interested in using (benzoic acid) chromium tricarbonyl[40,41] as starting material. Our intention is to study the influence of the organometallic compound on the formation process and the structure of the polymer in a systematic way. Further derivatization of the chromium tricarbonyl unit by classical thermal or photolytic activation methods seem to be possible. Since (arene) chromium tricarbonyl 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) chromium tricarbonyl and (η^6-1,4-benzenedicarboxylate) chromium tricarbonyl. These compounds already form one and two-dimensional networks in the solid state.[42] In contrast to ferrocenyl substituted carboxylate coordination polymers,[20,43,44] to the best of our knowledge no systematic investigations have been performed with (η^6-benzenecarboxylate) chromium tricarbonyl as metallo ligands.

Herein we report on the reaction of $[\{\eta^6\text{-}C_6H_5COOH\}Cr(CO)_3]$ with zinc acetate in the presence of various organic dipyridyl linkers. Depending on the nature of the linker either monomeric or polymeric compounds were obtained.

Experimental Section

General Procedures. Deuterated solvents were obtained from Aldrich (99 atom % D). NMR spectra were recorded on 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 on a Bruker FTIR Tensor 37 via the Attenuated Total Reflection method (ATR). Elemental analyses were carried out with an Elementar vario EL. Thermogravimetric analysis (TGA) measurements were made on a Netzsch STA 429 instrument. The solvents were used as purchased from commercial sources without further purification. $[\{\eta^6\text{-}C_6H_5COOH\}Cr(CO)_3]$ was prepared according to literature procedures.[29,30]

$[Zn[\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3]_2(4,4'\text{-bipy})]_n$ (1). To a solution of $[Zn(CH_3COO)_2\cdot(H_2O)_2]$ (44 mg; 0.200 mmol) in a dimethylformamide (DMF)/methanol mixture, $[\{\eta^6\text{-}C_6H_5COOH\}Cr(CO)_3]$ (101 mg; 0.400 mmol) was added. The solution was stirred for 1 h, and then 4,4′-bipyridine (31 mg; 0.200 mmol) was added. The subsequent mixture was stirred for another 6 h. While stirring a yellowish orange precipitate was formed. The precipitate was dissolved by heating and kept for crystallization. Within one day yellowish orange crystals were formed. Yield: 105 mg. (71% based on Zn). Anal. Calcd for $C_{30}H_{18}Cr_2N_2O_{10}Zn$: C, 48.97; H, 2.47; N, 3.81 Found: C, 47.78; H, 2.62; N, 4.17. ^1H NMR (DMSO-d_6, 300 MHz, 25 °C): δ (ppm) 8.77 (4H, br, Ar), 7.49 (4H, br, Ar), 6.26 (4H, m, Ar), 5.87 (2H, m, Ar), 5.69 (4H, m, Ar). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz, 25 °C): δ (ppm) 233.2 (CO), 168.8 (COO), 150.5 (Py), 144.7 (Py), 121.6 (Py), 98.8 (Ar), 97.2 (Ar), 96.8 (Ar), 93.1 (Ar). IR: υ = 3072 (b), 2363 (s), 2335 (s), 2160 (b), 1956 (s), 1866(s), 1677 (sh), 1606 (s), 1496 (s) 1453 (sh), 1411 (sh), 1390(sh), 1357 (s), 1222(s), 1141 (s) 1068 (s), 1044 (sh), 1011 (s), 847 (sh), 818 (s), 786 (s), 721 (s), 689 (s), 657 (s) 622 (s), 568 (s), 531 (s) cm^{-1}.

$[Zn[\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3]_2(bpe)]_n$ (2). To a solution of $[Zn(CH_3COO)_2\cdot(H_2O)_2]$ (44 mg; 0.200 mmol) in DMF, $[\{\eta^6\text{-}C_6H_5COOH\}Cr(CO)_3]$ (101 mg; 0.400 mmol) was added. The subsequent mixture was stirred for 1 h. Then, 1,2-bis(4-pyridyl)ethane (37 mg; 0.200 mmol) was added, and the solution was stirred for another 6 h. While stirring a yellowish orange precipitate was formed. The precipitate was dissolved by heating and kept for crystallization. Within one day yellow crystals were formed. Yield: 135 mg. (74%). Anal. Calcd for $C_{38}H_{36}Cr_2N_4O_{12}Zn$: C, 50.15; H, 3.98; N, 6.17 Found: C, 50.37; H, 4.23; N, 6.44. ^1H NMR (DMSO-d_6, 300 MHz, 25 °C: δ (ppm) 8.50 (4H, br, Ar), 7.34 (4H, br, Ar), 6.26 (4H, m, Ar), 5.87 (2H, m, Ar), 5.69 (4H, m, Ar), 2.89 (4H, s, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz, 25 °C): δ (ppm) 233.3 (CO), 168.8 (COO), 151.0 (Py), 149.3 (Py), 124.3 (Py), 98.9 (Ar), 97.2 (Ar), 96.8 (Ar), 93.2 (Ar), 35.8 (CH_2). IR: υ = 2929 (b), 2362 (s), 2335 (s), 2159(b), 2019 (b), 1955 (s), 1853(s), 1663 (s), 1617 (s), 1565 (sh), 1503 (s), 1431 (sh), 1384 (sh), 1351 (s), 1255 (s), 1148 (s), 1085 (s), 1032 (sh), 888 (s), 838 (s), 782 (s), 722 (s), 686 (s), 661 (s), 628 (s), 532 (s) cm^{-1}.

$[Zn[\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3]_2(tmdp)\}]_n$ (3). To a solution of $[Zn(CH_3COO)_2\cdot(H_2O)_2]$ (44 mg; 0.200 mmol) in DMF, $[\{\eta^6\text{-}C_6H_5COOH\}Cr(CO)_3]$ (101 mg; 0.400 mmol) was added. The subsequent mixture was stirred for 1 h. Then 1,3-bis(4-pyridyl)propane (40 mg; 0.200 mmol) was added, and the solution was stirred for another 6 h. While stirring a yellow precipitate was formed. The precipitate was dissolved by heating and kept for crystallization. Yield: 100 mg. (62%). Anal. Calcd for $C_{33}H_{24}Cr_2N_2O_{10}Zn$: C, 50.95; H, 3.11; N, 3.60, Found: C, 50.98; H,

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Table 1. Crystallographic Details of **1**−**4**

	1	**2**	**3**	**4**
chemical formula	$C_{60}H_{36}Cr_4N_4O_{20}Zn_2$	$C_{32}H_{22}Cr_2N_2O_{10}Zn \cdot 2(C_3H_7NO)$	$C_{66}H_{48}Cr_4N_4O_{20}Zn_2 \cdot H_2O$	$C_{30}H_{19}Cr_2N_3O_{10}Zn \cdot CHCl_3$
formula mass	1471.67	910.08	1573.84	870.22
space group	$P\bar{1}$	$Pna2_1$	C_2	$P\bar{1}$
a/Å	13.857(3)	21.705(4)	19.1846(6)	11.5244(4)
b/Å	15.846(3)	6.2555(13)	14.7042(5)	12.5316(5)
c/Å	15.878(3)	29.712(6)	12.3100(4)	13.4182(6)
α/deg	103.41(3)	90.00	90.00	95.948(3)
β/deg	111.20(3)	90.00	111.921(2)	96.497(3)
γ/deg	108.42(3)	90.00	90.00	114.688(3)
unit cell volume/Å^3	2838.1(10)	4034.1(14)	3221.5(2)	1724.80(12)
temperature/K	200(2)	200(2)	200(2)	200(2)
Z	2	4	2	2
radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ/mm^{-1}	1.655	1.185	1.465	1.601
no. of reflections measured	25573	26231	15514	21068
no. of independent reflections	10064	7205	8606	7298
R_{int}	0.0659	0.0960	0.0909	0.0547
final R_1 values ($I > 2\sigma(I)$)	0.0586	0.0462	0.0485	0.0432
final $wR(F^2)$ values (all data)	0.2229	0.1031	0.1266	0.1287
goodness of fit on F^2	0.980	0.924	1.018	1.040

3.36; N, 3.58. ^{1}H NMR (DMSO-d$_6$, 300 MHz, 25 °C): δ (ppm) 8.50 (4H, br, Ar), 7.42 (4H, br, Ar), 6.26 (4H, m, Ar), 5.87 (2H, m, Ar), 5.69 (4H, m, Ar), 2.66 (4H, m, CH_2), 1.95 (2H, m, CH_2). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 75 MHz, 25 °C): δ (ppm) 233.3 (CO), 168.9 (COO), 152.0 (Py), 149.3 (Py), 124.3 (Py), 98.8 (Ar), 97.2 (Ar), 96.8 (Ar), 93.2 (Ar), 33.8 (Py-CH_2−CH_2), 29.9 (Py-CH_2-CH_2). IR: υ = 3068 (b), 2363 (s), 2335 (s), 2161 (b), 1953 (s), 1857 (s), 1603 (s), 1522 (sh), 1503 (s), 1429 (sh), 1410 (sh), 1361 (s), 1225 (s), 1141 (s), 1068 (s), 1027 (s), 883 (sh), 832 (sh), 817 (s), 789 (s), 725 (sh), 687 (s), 660 (s), 622 (s), 576 (sh), 530 (s) cm^{-1}.

[Zn[{η^6-C_6H_5COO}Cr(CO)$_3$]$_2$(DPA)] (4). [Zn($CH_3COO)_2 \cdot (H_2O)_2$] (44 mg; 0.200 mmol) and 2,2′-dipyridylamine (34 mg; 0.200 mmol) were dissolved in methanol (20 mL) and stirred for 1 h. To this solution [{η^6-C_6H_5COOH}Cr(CO)$_3$] (101 mg; 0.400 mmol) was added and subsequent mixture was stirred for 6 h. While stirring a yellow-colored precipitate was formed. The precipitate was isolated by filtration, dissolved in a chloroform and methanol mixture, and kept for crystallization. After 1 day yellow crystals were obtained. Yield: 150 mg. (79%). Anal. Calcd for $C_{30}H_{19}Cr_2N_3O_{10}Zn$ (corresponds to the loss of one chloroform): C, 47.98; H, 2.55; N, 5.60; Found: C, 48.20; H, 2.73; N, 5.68. ^{1}H NMR (DMSO-d$_6$, 300 MHz, 25 °C): δ (ppm) 8.34 (2H, d, J = 6 Hz, Ar), 7.83 (2H, m, Ar), 7.43 (2 H, d, J = 6 Hz, Ar), 7.03 (2H, t, J(H, H) = 6 Hz, Ar), 6.19 (4H, d, J(H, H) = 6 Hz, Ar), 5.80 (2H, t, J(H, H) = 6 Hz, Ar), 5.65 (4H, t, J(H, H) = 6 Hz, Ar). ^{13}C{^{1}H} NMR (DMSO-d$_6$, 75 MHz, 25 °C): δ (ppm) 233.2 (CO), 169.1 (COO), 153.7 (Py), 146.8 (Py), 139.8 (Py), 127.9 (Py), 116.8 (Py), 98.9 (Ar), 97.0 (Ar), 96.6 (Ar), 93.3 (Ar). - IR: υ = 3086 (b), 2160 (b), 2027 (sh), 1955 (s), 1861 (s), 1650 (s), 1586 (s), 1530 (sh) 1482 (s), 1418 (sh), 1373 (s), 1273 (sh), 1234 (s), 1158 (s), 1050 (s), 1015 (s), 962 (sh), 909 (sh), 880 (s), 831 (s), 767 (s), 725 (sh), 686 (s), 657 (s), 623 (s), 528 (s) cm^{-1}.

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 −73 °C cold stream of a STOE IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Core2Duo PC.

All structures were solved by the Patterson method (SHELXS-97[45]). The remaining non-hydrogen atoms were located from successive difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[45] Carbon-bound hydrogen atom positions were calculated. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. 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. Positional parameters, thermal parameters, bond distances, and angles have been deposited as Supporting Information.

Results and Discussion

To understand the formation of various zinc coordination polymers with (η^6-benzenecarboxylate) chromium tricarbonyl as metallo ligands dipyridine bases were used as organic likers to build the polymeric network. Different spacers between the two pyridine moieties were used to vary the distance between the zinc atoms. Reactions of (benzoic acid) chromium tricarbonyl with zinc acetate and the dipyridine based ligands 4,4′-bipyridine (4,4′-bipy), 1,2-bis(4-pyridyl)ethane (bpe), and 1,3-bis(4-pyridyl)propane (tmdp) afforded the novel coordination polymers [Zn[{η^6-C_6H_5COO}Cr(CO)$_3$]$_2$(4,4′-bipy)]$_n$ (**1**), [Zn[{η^6-C_6H_5COO}Cr(CO)$_3$]$_2$(bpe)]$_n$ (**2**), and [Zn[{η^6-C_6H_5COO}Cr(CO)$_3$]$_2$(tmdp)}]$_n$ (**3**) in good yields (Scheme 1). Compounds **1**−**3** contain (η^6-benzenecarboxylate) chromium tricarbonyl as building block. All three compounds were characterized by standard analytical/spectroscopic techniques, and the solid state structures were determined by single crystal X-ray diffraction.

The ^{1}H NMR spectra of compounds **1**−**3** show two signals for the pyridine rings (δ 8.77 and 7.49 ppm (**1**), 8.50 and 7.34 ppm (**2**), and 8.50 and 7.42 ppm (**3**)) and three signals for the benzenecarboxylate unit in the range of δ 6.26 to 5.69 ppm. Moreover, the expected signals for the alkyl bridges were observed for compound **2** and **3** (δ 2.89 ppm (**2**), 2.66 and 1.95 ppm (**3**)). The ^{13}C{^{1}H} NMR spectra of all compounds show the expected sets of signals. The characteristic signal of the carbonyl groups were seen at δ 233.12 ppm. The signals of the carboxylate groups were observed around δ 169.3 ppm. In the IR spectra the A_1 and E νCO stretching frequencies were measured at 1956 cm^{-1}, 1866 cm^{-1} (**1**), 1955 cm^{-1}, 1853 cm^{-1} (**2**), and 1953 cm^{-1}, 1857 cm^{-1} (**3**).

Crystals of compounds **1**−**3** were grown in the dark because of the light sensitivity of the reaction mixture. When exposed to daylight they decomposed and changed their color.

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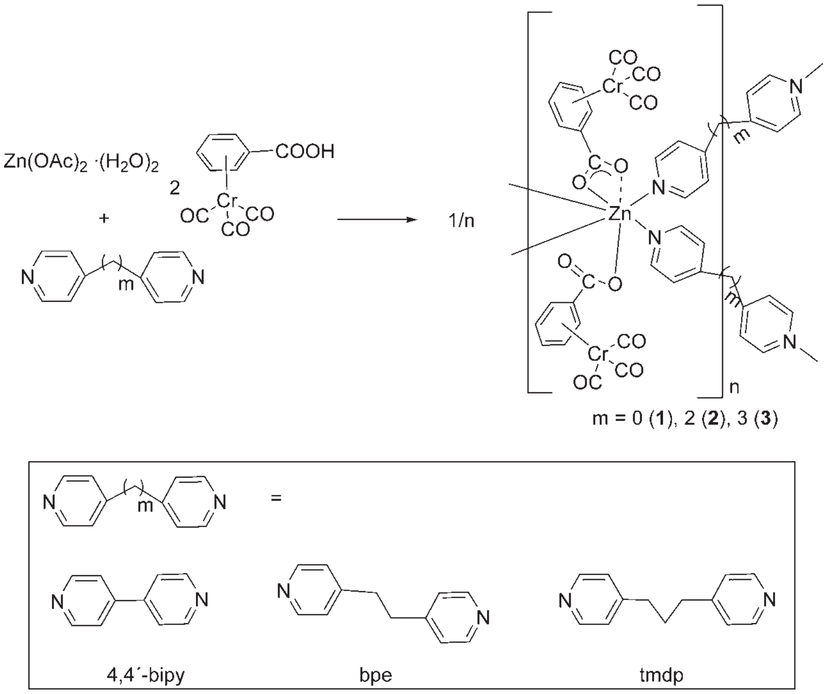
Scheme 1



Compound **1** crystallizes in the triclinic space group with $P\bar{1}$. Data collection parameters and selected bond lengths and angles are given in Table 1 and in the captions of Figures 1. The asymmetric unit consists of two zinc atoms (Zn1, Zn2) and four carboxylate anions (Cr1, Cr2, Cr3, and Cr4) and two 4,4′-bipyridine ligands (Figure 1). The structure consists of a one-dimensional (1D) zigzag chain polymer, in which the $[Zn[\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3]_2]$ units are connected by 4,4′-bipyridine ligands. Each zinc atoms adopts a distorted square pyramidal coordination environment which is formed by three oxygen atoms (O1, O2, and O6 for Zn1 and O11, O16, and O17 for Zn2) from two carboxylate $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anions and two nitrogen atoms from the bridging 4,4′-bipyridine ligands (N1 and N4 for Zn1; N2 and N3 for Zn2). One of these pyridyl nitrogen atoms (N1 and N2, respectively) is located in the axial position. Interestingly, the carboxylate $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anions display two different coordination modes (κ^1 and κ^2) resulting in the penta-coordinated zinc atoms. The Zn−N bond distances range from 2.054(7) Å to 2.100(8) Å, while Zn−O bond distances range between 1.957(7) Å and 2.085(9) Å. The distances between the two zinc atoms is 11.294(3) Å. The two different 4,4′-bipyridine ligands of each zinc atom are located in an almost rectangular arrangement (N1−Zn1−N4′ 99.6(3)°), which is important for the formation of the infinite zigzag chain. The structure of the polymer is in contrast to the corresponding ferrocenyl-substituted carboxylate complex $\{[Zn(o\text{-}OOCC_6H_4COFc)_2\text{-}(4,4'\text{-bipy})(H_2O)_2]\cdot 2MeOH\cdot 2\ H_2O\}_n$ (Fc = $(\eta^5\text{-}C_5H_5)Fe\text{-}(\eta^5\text{-}C_5H_4)$), which forms linear chains in the solid state.[20] In contrast, the zinc acetate polymer $[Zn_2(OAc)_2(4,4'\text{-bipy})]_n$ forms 1D molecular ladders, which are also different in comparison to compound **1**.[46,47] This shows that the nature of the organometallic compound has a significant influence on the structure of the polymer.

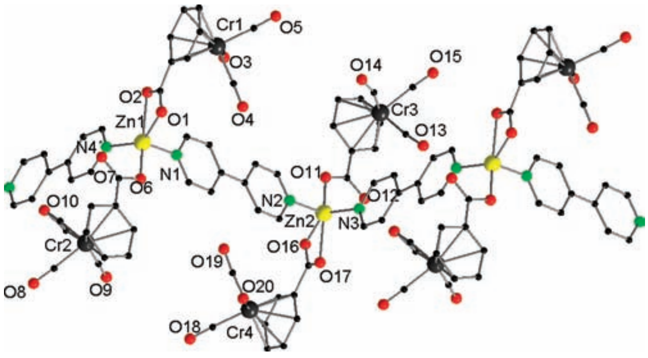


Figure 1. Solid-state structure of **1**, omitting hydrogen atoms. Selected distances [Å] and angles [deg]: Zn1−N1 Zn1 2.100(8), Zn1−N4′ 2.092(8), Zn2−N2 2.078(8), Zn2−N3 2.054(7), Zn1−O1 2.349(10), Zn1−O2 2.085(9), Zn1−O6 1.976(8), Zn2−O11 1.957(7), Zn2−O16 2.025(8), Zn2−O17 2.359(10); N1−Zn1−N4′ 99.6(3), N1−Zn1−O1 91.8(3), N1−Zn1−O2 104.3(3), N1−Zn1−O6 98.0(3), N4′−Zn1−O1 89.3(3), N4′−Zn1−O2 140.7(4), N4′−Zn1−O6 103.6(3), N2−Zn2−N3 99.8(3), N2−Zn2−O11 98.7(3), N2−Zn2−O16 104.6(3), N2−Zn2−O17 91.6(3), N3−Zn2−O11 102.4(3), N3−Zn2−O16 139.9(4), N3−Zn2−O17 89.6(3).

Compound **2** crystallizes in the orthorhombic space group $Pna2_1$ as a multiple twinned compound. Data collection parameters and selected bond lengths and angles are given in Table 1 and in the captions of Figures 2. The asymmetric unit of this molecule contains one zinc atom, two carboxylate $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anions, 1,2-bis(4-pyridyl)ethane, and two uncoordinated molecules of DMF (Figure 2, top). As observed for compound **1** the structure of compound **2** consists of 1D polymers, in which the $[Zn[\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3]_2]$ units are connected by 1,2-bis(4-pyridyl)ethane ligands. In contrast to compound **1** the zinc atom is only 4-fold coordinated. A slightly distorted tetrahedral coordination polyhedron is formed, in which the two carboxylate groups of the $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anion are only κ^1 coordinated via

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(46) Conerney, B.; Jensen, P.; Kruger, P. E.; Moubaraki, B.; Murray, K. S. *CrystEngComm* **2003**, *5*, 454–458.

(47) Kim, J.; Lee, U.; Koo, B. K. *Bull. Korean Chem. Soc.* **2006**, *27*, 918–919.

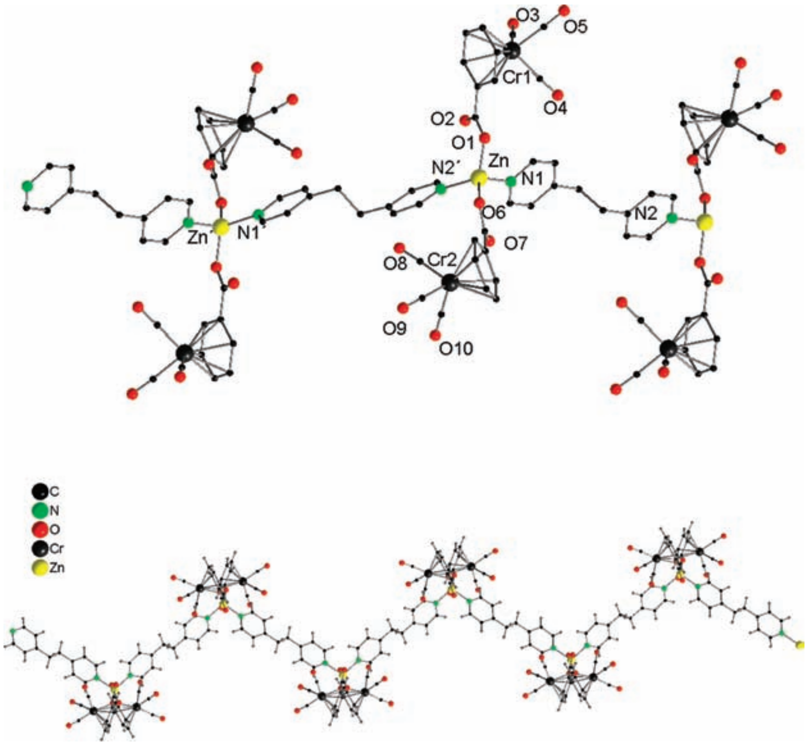

Figure 2. Solid-state structure of **2**, omitting hydrogen atoms. Top: three units of the polymeric chain. Bottom: cutout of the polymeric structure. Selected distances [Å] and angles [deg]: Zn−N1 2.022(4), Zn−N2′ 2.023(4), Zn−O1 1.960(4), Zn−O6 1.949(4); N1−Zn−O6 121.5(2), N1−Zn−O1 105.4(2), N2−Zn−O6 104.9(2), N2−Zn−O1 121.5(2), N1−Zn−N2 103.92(14), O1−Zn−O6 101.03(12).

the oxygen atoms (O1 and O6). The coordination sphere is completed by two nitrogen atoms (N1 and N2′) from two 1,2-bis(4-pyridyl)ethane ligands. Zn−N bond distances are Zn−N1 2.022(4) Å and Zn−N2′ 2.023(4) Å, while the Zn−O bond distances are Zn−O1 1.960(4) Å and Zn−O6 1.949(4) Å. The average bond angle of the ligands that are coordinated to the zinc atom is 109.7(2)° which is very close to the 109.5° for an ideal tetrahedron. As a result of the different coordination polyhedra the bond angles around the zinc atom are larger than in compound **1** (N1−Zn−N2′ 103.92(14)°). The thus formed polymeric zigzag chain is more open than in compound **1** (Figure 2, bottom) resulting in a distances of 13.149(2) Å between the two zinc atoms. A comparison of compound **2** and the zinc acetate polymer $[Zn(OAc)_2(bpe)]\cdot 2H_2O$ shows that in this case only slight differences in the structures are observed.[48] $\{[Zn(OAc)_2(bpe)]\cdot 2H_2O\}_n$ also forms a polymeric zigzag chain with a slightly more open N1−Zn−N2 angle of 106.59(1)° (103.92(14)° in **2**).

The enlargement of the distance between the two pyridyl units by inserting an ethane bridge in compound **2** does obviously not have a major influence on the structure. Therefore we next used 1,3-bis(4-pyridyl)propane as linker a in compound **3** to increase the distance between the pyridyl units even more. Compound **3** forms a helical structure in the solid state,[49] which is different from the previously described structures (Figure 3). It crystallizes in the monoclinic space group C_2 as a twin. Data collection parameters and selected bond lengths and angles are given in Table 1 and in the captions of Figures 3. The asymmetric unit consists of two carboxylate $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anions, one 1,3-bis(4-pyridyl)propane molecule, and one zinc atom (Figure 3). Moreover one uncoordinated water molecule is observed. In the solid state 1D polymers are formed. These consist of $[Zn[\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3]_2]$ units which are connected by 1,3-bis(4-pyridyl)propane ligands to give a helical chain (Figure 3). As observed for compound **2** the zinc atoms are slightly distorted tetrahedral coordinated by two oxygen atoms (O1 and O6) from κ^1 coordinated $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anions and two nitrogen atoms (N1 and N2) from two 1,3-bis(4-pyridyl)propane ligands. The Zn−N and Zn−O bond distances are within the expected range (Zn−N1 2.031(3) Å, Zn−N2 2.090(4) and Zn−O1 2.005(2) Å, Zn−O6 1.966(3) Å. The bond angles around the zinc atom range from 98.52(14)° to 137.08(15)°. The average bond angle is 108.66(15)° which is slightly smaller than 109.5° for an ideal tetrahedron. The distance between the two zinc atoms (12.556(2) Å) is significantly smaller than in compound **2** although a longer bridge between the pyridyl moieties was employed in compound **3**. This is a result of the folding of the polymer to a helical pattern. Beside the organic linkers, the $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anion also has an influence on the structure of the polymer. Chiral infinite double-stranded helical structures consisting of two single-stranded helices of the same handedness were obtained by using the 1,3-bis(4-pyridyl)propane linker and ZnI_2 as knot.[49] When zinc acetate was used as starting material in the presence of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4COO)]^-$ as metallo ligand, a 1D zigzag chain structure was obtained.[19]

Finally, we used the chelating ligand 2,2′ dipyridylamine (DPA) to obtain one monomeric complex to have a comparison with the polymeric compounds. The reaction of $[\{\eta^6\text{-}C_6H_5COOH\}Cr(CO)_3]$ with zinc acetate in the presence of DPA resulted in the monomeric compound $[Zn[\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3]_2(DPA)]$ (**4**) in good yield (Scheme 2). Compound **4** was characterized by standard analytical/

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[48] Ng, M. T.; Deivaraj, T. C.; Klooster, W. T.; McIntyre, G. J.; Vittal, J. J. *Chem.—Eur. J.* **2004**, *10*, 5853–5859.

[49] Han, L.; Valle, H.; Bu, X. *Inorg. Chem.* **2007**, *46*, 1511–1513.

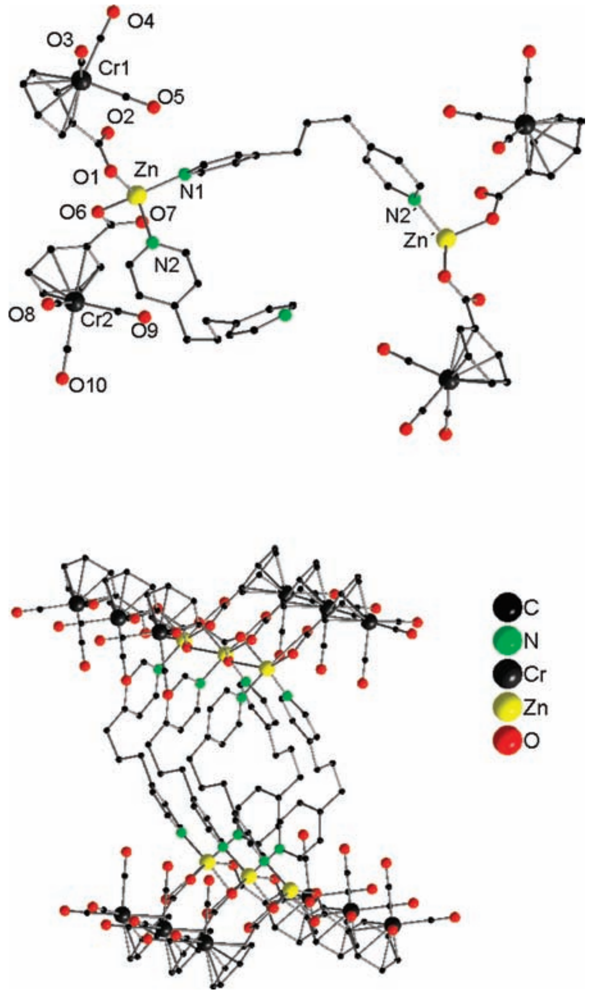
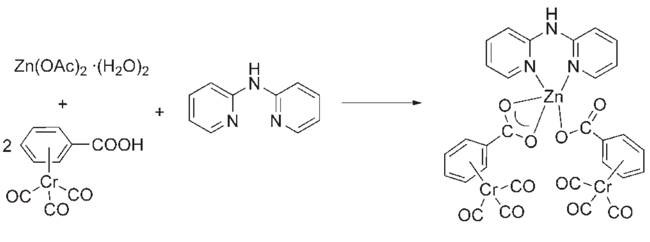


Figure 3. Solid-state structure of **3**, omitting hydrogen atoms. Top: one unit of the polymeric chain. Bottom: cutout of the helical structure. Selected distances [Å] and angles [deg]: Zn−N1 2.031(3), Zn−N2 2.090(4), Zn−O1 2.005(2), Zn−O6 1.966(3); N1−Zn−N2 98.52(14), N1−Zn−O1 111.71(12), N1−Zn−O6 137.08(15), N2−Zn−O1 103.69(12), N2−Zn−O6 100.09(14), O1−Zn−O6 100.87(12).

Scheme 2



4

spectroscopic techniques, and the solid state structure was determined by single crystal X-ray diffraction. The NMR data point to a symmetric coordination of the $\{\eta^6\text{-}C_6H_5\text{-}COO\}Cr(CO)_3$ anion in solution, which is in contrast to the solid state structure (see below). Obviously, there is a fluxional behavior of the ligands in solution. In the IR spectra the A_1 and E νCO stretching frequencies are observed at 1955 cm^{-1} and 1861 cm^{-1}(**4**).

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two moleclues of chloroform in the unit cell (Figure 4). Data collection parameters and selected bond lengths and angles are given in Table 1 and in the captions of Figure 4. The zinc atom is 5-fold coordinated forming a distorted square-pyramidal coordination polyhedron. The dipyridyl amine ligand coordinates via the pyridine nitrogen atoms N1 and N2 to the zinc atoms. Zn−N bond distances are Zn−N1 2.021(3) Å and Zn−N2 2.037(3) Å. As observed for compound **1** the carboxylate $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anions coordinate in a κ^1 and in a κ^2 mode to the zinc atom. This is in contrast to the symmetric pattern observed in the NMR spectra in solution.

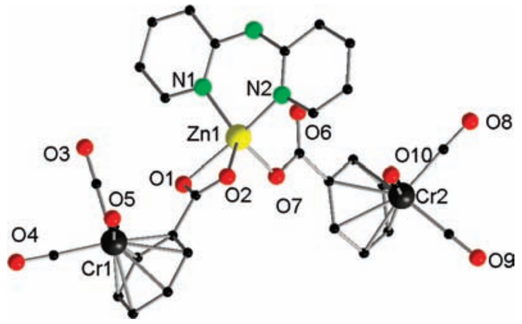


Figure 4. Solid-state structure of **4**, omitting hydrogen atoms. Selected distances [Å] and angles [deg]: Zn−N1 2.021(3), Zn−N2 2.037(3), Zn−O1 2.144(3), Zn−O2 2.245(3), Zn−O7 1.980(2); N1−Zn−O7 118.39(10), N2−Zn−O7 105.97(9), N1−Zn−N2 94.07(10), O1−Zn−O7 96.20(9), N1−Zn−O1 96.04(10), N2−Zn−O1 147.42(10), O7−Zn−O2 106.86(9), N1−Zn−O2 130.90(10), N2−Zn−O2 90.84(10), O1−Zn−O2 59.52(10).

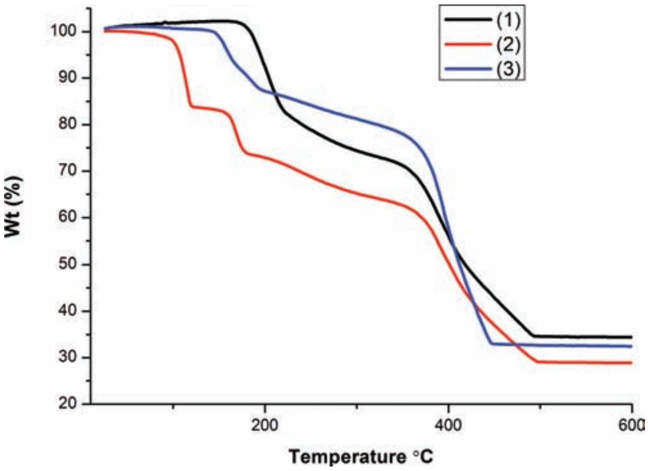


Figure 5. TGA curves for **1**−**3** in a temperature range between 25 and 600 °C at a heating rate of 5 °C/min under N_2 atmosphere.

TGA measurements were performed for the polymeric compounds **1**−**3** (Figure 5). Compound **1** is thermally relatively robust as shown by TGA. The decomposition starts at 178 °C. All 12 CO molecules (calculated for the asymmetric unit) were lost in the temperature range between 178 and 352 °C (obsd 29%, calcd 23%). Then, the product further decomposes at 495 °C with a weight loss of 36%, which is a result of the decomposition of the organic shell. The TGA curve of compound **2** shows the lost of two DMF molecules in the temperature range from 98 to 118 °C (obsd 16%, calcd 16%). Then the compound is stable up to 152 °C. As the temperature increases, decomposition starts and two weight losses are observed. The first weight loss was seen in the temperature range of 152 to 364 °C. Six CO molecules (calculated for the asymmetric unit) were lost (obsd 19% calcd 18%) in the first step. The product decomposed at 494 °C (32%) by losing its organic shell. The TGA curve of compound **3** has a comparable shape as the one of compound **1**. It shows that six CO and half of a water molecule (calculated for the asymmetric unit) are lost in the temperature range from 140 to 350 °C (obsd 22%, calcd 23%). Then as a result of the decomposition of the organic sphere a second step is observed to up to a temperature of 450 °C. The weight loss of this step is 45%. The loss of CO is in line with theoretical calculations.[39]

Summary

In summary, different coordination polymers of zinc with the organometallic ligand $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ were obtained by the reaction of $[\{\eta^6\text{-}C_6H_5COOH\}Cr(CO)_3]$ with zinc acetate in the presence of various organic dipyridyl linkers. Depending on the nature of the linker either monomeric or polymeric compounds were obtained. By using 1,3-bis(4-pyridyl)propane as linker a chiral infinite helical structure is formed in the solid state. The carboxylate $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anion coordinates in either a κ^1 or a κ^2 mode resulting in four and five-fold coordinated zinc atoms. The reported structures differ in comparison to coordination polymers of zinc without the metallo ligand $\{\eta^6\text{-}C_6H_5COO\}\text{-}Cr(CO)_3$ anion. TGA studies showed that upon heating the carbonyl groups of the $\{\eta^6\text{-}C_6H_5COO\}Cr(CO)_3$ anion are lost selectively before the organic ligand sphere is thermally decomposed.

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

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.