Bifunctional Aminotriphenolate Complexes as One-Component Catalysts for the ROCOP of Cyclic Anhydrides and Epoxides

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Abstract: Bifunctional aminotriphenolate complexes derived from trivalent metals (M = Co, Mn, Cr) have been prepared and structurally characterized. These complexes are octahedral in the solid state but infer dynamic behavior of the ligated dimethylaminopyridine (DMAP) ligands that can function as initiators in the ring-opening copolymerization of cyclic anhydrides and epoxides. More specifically, the ring-opening copolymerization of cyclohexene oxide and phthalic anhydride was studied in detail, and the bifunctional Cr(III) complex gave overall the best results in terms of overall activity and polyester quality.

Introduction

Polyesters are among the most widely used polymers in modern society being commonly applied as components of consumer plastics such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). The general industrial interest in polyesters finds its origin in their appealing properties, such as good mechanical strength as well as high abrasion- and chemical-resistance. Such features make polyesters good candidates to be used in multiple applications ranging from bulk packaging to coatings and fibers. Consequently, the preparation of polyesters and the development of efficient and sustainable synthetic routes have attracted the interest of many industrial and academic scientists.[1]

In this context, alternating ring-opening copolymerization (ROCOP) of epoxides and anhydrides is considered a powerful strategy to prepare polyesters.[1g-i] This promising route enables the controlled transformation of generally accessible and versatile monomers into polyesters under mild conditions. Also, and unlike for the ring-opening polymerization (ROP) of lactones, the use of monomers containing a range of functional groups is often tolerated and thus ROCOP provides an efficient way to produce polyesters with wide-ranging properties and diverse architectures.

Since the pioneering work of Inoue[2] who reported on an Al(III)-porphyrin complex as catalyst for ROCOP, numerous other catalyst systems have been developed to improve the yield, selectivity and polymer properties including narrow polydispersities and increased molecular weights. In the current realm of ROCOP, Co(III)salen and Cr(III) complexes are privileged catalysts showing high efficiency.[3] Combined with the Inoue contributions, these seminal results inspired the development of other bifunctional and binary catalytic systems based on different metals including Zn,[3e,4] Mg,[4b] Mn,[5] Al,[6] and Fe.[7] Often the metal ions are supported by multidentate ligands[8] that allow for the possibility to tune the steric and electronic features of the catalysts.

We have become recently interested in the development of new catalytic systems for ROCOP processes that involve epoxide substrates.[9] As alternative ligands, we considered that aminotriphenolates would offer additional epoxide activation potential as these ligands are geometrically more flexible and should also allow for coordination of sterically more demanding substrates (Figure 1). Due to these favorable flexibility features and switchable coordination behavior around the metal center allowing for both penta- and hexa-coordinated structures (Figure 1),[10] the aminotriphenolate complexes are promising candidates for catalytic applications as has recently been reported.[11] Additionally, complexes containing diamino(bisphenolate) and amino(triphenolate) ligands have also gained attention in ring opening polymerization (ROP) of lactides,[12] and copolymerization reactions between epoxides and CO_2.[13]

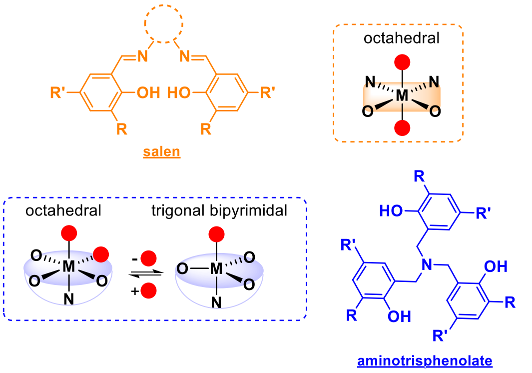

Figure 1. Preferred coordination geometries for M(III)-based complexes based on salen (orange) or aminotriphenolate ligands (blue).

In a recent contribution we reported on the synthesis and structural features of Co(II) and Co(III) aminotriphenolate complexes.[14]Interestingly, the Co(III) complexes containing two *cis*-ligating dimethylamino-pyridine (DMAP) ligands showed reversible coordination of one of these ligands in solution under ambient conditions providing thus simple access to coordinative unsaturated Co(III) aminotriphenolates and one free DMAP.

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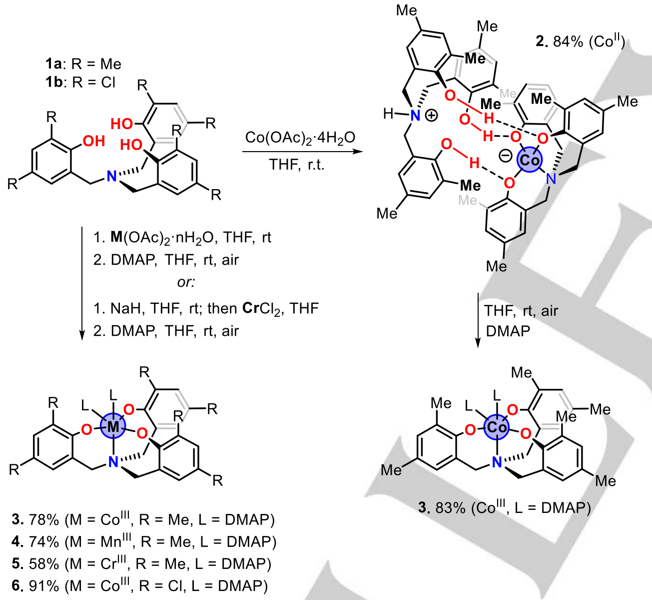
Herein, we will show that this reversible coordination behavior of DMAP allows to use these Co(III) and its Mn(III) and Cr(III) congeners as bifunctional catalysts, with the free DMAP acting as a nucleophilic initiator of the alternating ROCOP between epoxides and phthalic anhydride (PA) producing polyesters. The influence of the structural identities of the complexes and the type of metal ions on the reactivity in these ROCOP process is also discussed.

Results and Discussion

Synthesis and Characterization of Complexes

Scheme 1 summarizes the synthesis of complexes **2**–**6** from aminotriphenolate ligands **1**. Co(III) complex **3** was prepared as previously described,[14] and this provided a starting point for the synthesis of Mn(III) complex **4** and Cr(III) complex **5**. Whereas **2** was shown to be a precursor to Co(III) **3**, the latter may also be directly prepared from **1** by combining an equimolar amount of $Co(OAc)_2·4H_2O$ and ligand **1** followed by the addition of an excess of DMAP in the presence of air. This afforded Co(III) complex **3** in 78 % yield after recrystallization from CH_2Cl_2/hexane.



Scheme 1. Synthesis of aminotriphenolate complexes **2**–**6** (M = Co(III), Mn(III) and Cr(III)) from precursor ligand **1**.

Analogously, Mn(III) complex **4** was prepared from a mixture of $Mn(OAc)_2·4H_2O$ and ligand **1** in a 1:1 ratio at rt in the presence of DMAP and air to provide a brown solid that after recrystallization from THF gave **4** in 74 % yield. The first step of the synthesis of **4** (i.e., the reaction between the metal precursor and ligand **1**) was performed under N_2 due to the unstable nature of the intermediate Mn(II) complex. The corresponding Cr(III) complex **5** was prepared in a similar way by first deprotonating ligand **1** using NaH following transmetalation by $CrCl_2$under inert N_2. The final Cr(III) complex was then furnished by addition of DMAP in air providing complex **5** as a light purple powder. Recrystallization from CH_2Cl_2 gave the pure complex in 58% yield. The chlorinated Co(III) complex **6** was similarly prepared and isolated in 91% yield as a red/purple solid.

Single-crystal X-ray diffraction studies of crystalline **4**–**6** were performed to further confirm their proposed connectivities (see Figure 2 and Supporting Information).[15] Complexes **4**–**6** present isostructural coordination geometries compared to previously reported Co(III) complex **3**, with the aminotriphenolate acting as a tetradentate ligand with the O-atoms occupying three equatorial positions around the metal center, and two DMAP ligands occupying an equatorial and axial position, respectively.[16]

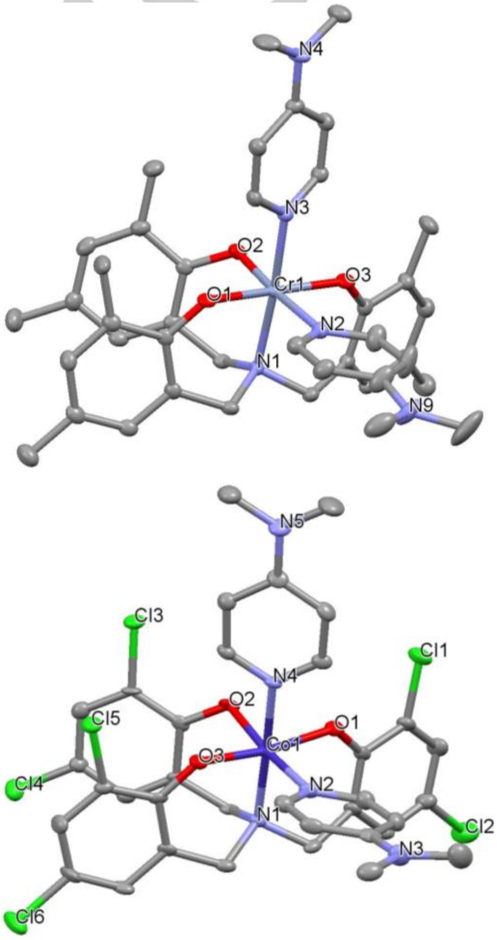


Figure 2. X-ray molecular structures measured for Cr(III) complex **5**and Co(III) complex **6** with esd´s in parentheses. Pertinent bond lengths (Å)/angles (º) for **5**: Cr1-O1 = 1.943(2), Cr1-O2 = 1.934(2), Cr1-O3 = 1.942(2), Cr1-N1 = 2.140(3), Cr1-N2 = 2.155(3), Cr1-N3 = 2.094(3); O2-Cr1-N2 = 175.65(10), O1-Cr1-O3 = 174.53(10), N1-Cr1-N3 = 175.99(10), N2-Cr1-N3 = 89.30(10), O2-Cr1-O3 = 90.04(10). Pertinent bond lengths/angles for **6**: Co1-O1 = 1.889(3), Co1-O2 = 1.918(3), Co1-O3 = 1.899(3), Co1-N1 = 2.026(4), Co1-N2 = 2.011(4), Co1-N4 = 1.966(4); O2-Co1-N2 = 173.71(15), O1-Co1-O3 = 171.03(14), N1-Co1-N4 = 178.21(16), N1-Co1-N2 = 93.46(16), O1-Co1-O2 = 87.38(14).

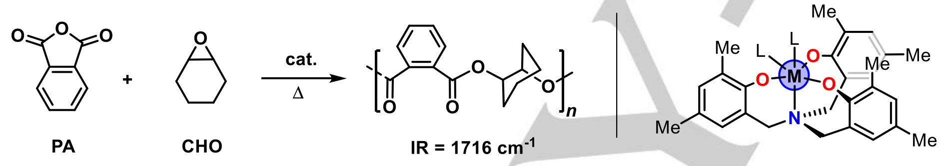
Despite the six-coordinate behavior in the solid state, both complexes **4** (M = Mn^{III}; 3d^4) and **5** (M = Cr^{III}; 3d^3) display paramagnetic NMR characteristics as may be expected from their electronic configurations. This behavior is in line with the NMR observations previously done for Co-complex **3**. The latter showed fluxional behavior in the DMAP coordination, with a preference for a six-coordinate, low-spin diamagnetic (Co^{III}; 3d^6) species at temperatures < −20 ºC. In contrast to **4** and **5**, the ^{1}H NMR spectrum of chloride-substituted Co-complex **6** displays a diamagnetic species, which may be explained by a lower tendency of this complex to equilibrate between five- and six-coordinate Co (Figure 1) due to the higher Lewis acidity of the metal ion. Such effects may affect catalytic ROCOP performance, where the presence of a free nucleophile (DMAP) is warranted for initiation of the polymerization process (*vide infra*).

ROCOP using CHO and PA

Initially we compared the catalytic abilities of complexes **3**-**6** in the coupling of 1,2-epoxyhexane and maleic anhydride (MA). From these initial experiments, it became clear that the Co-complex **6** appended with peripheral chloride substituents showed hardly any catalytic behavior. Therefore, in the subsequent copolymerization studies this complex was not further investigated (see Supporting Information for details). This is in line with the diamagnetic character of **6** observed in the NMR analysis, and the (slightly) shorter Co-N(DMAP) distances noted for **6** (2.011 and 1.966 Å) as compared to **3** (2.035 and 1.978 Å).[14]

Next, we focused our attention on the copolymerization of the benchmark substrates cyclohexene oxide (CHO) and phthalic anhydride (PA) using bifunctional complexes **3**–**5** as catalysts (Table 1). Previously we reported on the Fe-catalyzed copolymerization of polyesters from various (biobased) cyclic anhydrides and epoxides,[7b,c] and this provided a starting point for the present studies (65 ºC, 0.25 mol% catalyst loading). Whereas the Co-based and Mn-centered (aminotriphenolate) complexes **3** and **4** showed only low copolymerization potential (entries 1 and 2), the Cr-derivative **5** displayed significantly higher activity at 65

Table 1. Copolymerization of PA and CHO mediated by bifunctional complexes **3**–**5**(M = Co, Cr or Mn) under various reaction conditions. DCE stands for 1,2-dichloroethane, Tol = toluene.[a]

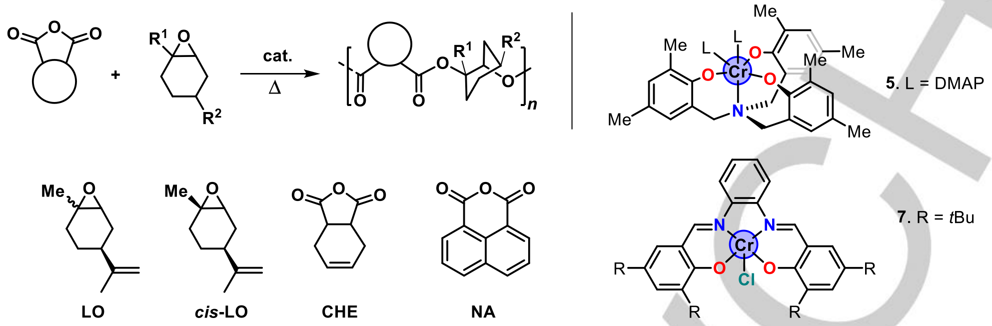


3. M = Co, L = DMAP
4. M = Mn, L = DMAP
5. M = Cr, L = DMAP

Entry	Complex [mol%]	CHO/PA	Solvent [PA in M]	T [ºC]	Conversion [%][b]	Ether [%][b]	M_n [Kg/mol][c]	Ð [c]	T_g [ºC][d]
1	**3**, 0.25	1.1:1	THF (8 M)	65	18	–	–	–	–
2	**4**, 0.25	1.1:1	THF (8 M)	65	20	–	–	–	–
3	**5**, 0.25	1.1:1	THF (8 M)	65	69	<1	7.6	1.15	130
4	**5**, 0.50	1:1	THF (8 M)	65	87	<1	9.9	1.13	133, 143
5	**5**, 0.50	1.1:1	THF (8 M)	65	83	2	9.5	1.46	134
6	**5**, 0.50	2:1	THF (8 M)	65	>99	3	11.2	1.16	135
7	**5**, 0.50	4:1	neat	65	>99	5	9.3	1.12	132
8	**5**, 0.50	1:1	DCE (8 M)	65	70	2	2.8	1.44	108
9	**5**, 0.50	1:1	Tol (8 M)	65	65	3	14.8	1.24	138
10[e]	–	1:1	THF (8 M)	65	47	<1	6.4	1.15	132
11[f]	**5**, 0.50	1:1	THF (8 M)	100	81	<1	9.8	1.32	132
12	**5**, 0.50	1.1:1	Tol (8 M)	85	83	<1	11.1	1.39	138
13	**5**, 0.50	1:1	Tol (8 M)	110	95	3	18.4	1.47	144

[a] Reaction conditions: 4.0 mmol PA, complexes **3**, **4** or **5**; 15 h reaction time unless stated otherwise. [b] Determined by ^{1}H NMR analysis ($CDCl_3$) of the crude reaction mixture; “Ether” stands for amount of ether linkages. [c] Determined by gel permeation chromatography (GPC) analysis in THF and using polystyrenes as calibration standards. [d] Determined by differential scanning calorimetry (DSC). [e] Using DMAP (0.50 mol%) as catalyst. [f] Reaction time was 24 h.

Table 2. Comparison between the efficiency of bifunctional Cr-complex **5** and a Cr(salphen) complex **7**/DMAP binary catalyst in the copolymerization of PA and CHO, and evaluation of other epoxides and cyclic anhydride combinations using **5** as catalyst. PPNCl stands for bis(triphenylphosphine)iminium chloride.[a]



Entry	Complex [mol%]	CHO/PA	Solvent [PA in M]	T [ºC]	Conversion [%][b]	Ether [%][b]	M_n [Kg/mol][c]	Đ [c]	T_g [ºC][d]
1	**5**, 0.25	1.1:1	THF (8 M)	65	69	<1	7.6	1.15	130
2	**5**, 0.50	1.1:1	Tol (8 M)	85	83	2	11.1	1.39	138
3[e]	**7**, 0.25	1.1:1	THF (8 M)	65	99	<1	12.8	1.19	142
4[f]	**7**, 0.25	1.1:1	THF (8 M)	65	>99	<1	17.0	1.28	143
5[g]	**5**, 0.50	1.1:1	Tol (8 M)	85	68	4	5.9	1.31	113
6[h]	**5**, 0.50	1.1:1	Tol (8 M)	85	95	<1	5.1	1.32	105
7[i]	**5**, 0.50	1.1:1	Tol (8 M)	85	99	12	2.0	1.15	89
8[j]	**5**, 0.50	1.1:1	Tol (8 M)	85	41	<1	6.2	1.65	140

[a] Reaction conditions: 4.0 mmol PA, complexes **3**, **4** or **5**; 15 h reaction time unless stated otherwise. [b] Determined by ^{1}H NMR analysis ($CDCl_3$) of the crude reaction mixture; "Ether" stands for amount of ether linkages. [c] Determined by gel permeation chromatography (GPC) analysis in THF and using polystyrenes as calibration standards. [d] Determined by differential scanning calorimetry (DSC). [e] Using also DMAP (0.25 mol%) as additive. [f] Using also PPNCl (0.25 mol%) as additive. [g] LO as substrate, reaction time 48 h. [h] *cis*-LO as substrate, reaction time 30 h. [i] Using CHE as substrate, reaction time 42 h. [j] Using NA as substrate, reaction time 30 h.

ºC (entry 3), and the isolated poly(CHO-*alt*-PA) was of high quality as testified by the chemoselectivity of the process (>99% ester linkages) and the low polydispersity (Đ = 1.15). The molecular weight of this polymer was moderately high (7.6 Kg/mol), and therefore further attempts were done to improve these features.

The ratio between CHO and PA was then varied between 1:1 up to 4:1 (entries 4-7), resulting in some cases in higher PA conversion levels and consequently higher molecular weights up to 11.2 Kg/mol. When a 4:1 CHO/PA ratio was used, the reaction could be performed under "neat" conditions but did not result in better polymer properties (entry 7). The glass transition temperature (T_g) of the alternating copolymer increased up to 135 ºC for the highest molecular weight in this series of experiments (entries 1-7). Changing the solvent to 1,2-dichloroethane (DCE, entry 8) was detrimental to the quality of the copolymer and only oligomeric product with a relatively low glass transition (M_n = 2.2 Kg/mol, Đ = 1.44 ºC, T_g = 108 ºC) was obtained. The use of toluene (entry 9) under similar conditions compared to the reaction carried out in THF (entry 4), however, proved to be beneficial as significantly higher molecular weight material (M_n = 14.8 Kg/mol, Đ = 1.24, T_g = 138 ºC) and a slightly higher glass transition were noted. Higher reaction temperatures were also probed (entries 11-13) using either THF or toluene as the medium, and the best results were finally obtained at 110 ºC (entry 11, toluene as solvent; M_n = 18.4, Đ = 1.47, T_g = 144 ºC). It should be noted that the reaction in the absence of a Lewis acid (no Cr present, entry 10; only with 1.0 mol% DMAP) also proceeded towards a copolymer though with a much lower efficiency. It is reasonable to assume that only one DMAP of Cr-complex **5** is involved in the monomer activation, and therefore the result obtained in the presence of DMAP only may be to some extent overestimated. Evidence for DMAP initiation was found by analyzing the isolated polymer from entry 3 in Table 1 by MALDI-TOF mass spectrometry (see Supporting Information), showing that the main peak distributions indeed have a DMAP molecule incorporated.

ROCOP using various Epoxides and Cyclic Anhydrides

To benchmark the results obtained for **5** in the copolymerization of CHO and PA, we compared the data against those obtained with a binary system comprising of the Cr(salphen) complex **7** and DMAP (Table 2, entries 1-4).[17] Though similar order molecular weights and T_g´s for the poly(CHO-*alt*-PA) polymers can be achieved, the use of complex **7** proved to be more effective as lower loadings of the complex and DMAP (0.25 mol%) were required (entry 2 versus 3). The Cr(salphen) based binary system in combination with bis(triphenylphosphine)iminium chloride (PPNCl) gave further improved results with an increase in the molecular weight to 17.0 Kg/mol (entry 4). Nonetheless, the comparison suggests that easily prepared bifunctional Cr(III) catalysts such as **5** comprising built-in nucleophiles (DMAP) are effective catalysts with appreciable activity in the formation of polyesters from cyclic anhydrides and epoxides, and relatively high glass transitions beyond 140 ºC.[4d]

Next, we examined whether Cr-complex **5** had potential towards the formation of various copolymers based on different epoxide/cyclic anhydride monomers as depicted in Table 2. First *cis/trans*-limonene oxide (*cis/trans* = 40:60) was examined and poly(LO-*alt*-PA) was produced at 85 ºC with a moderate molecular weight (entry 5; M_n = 5.9 Kg/mol) and T_g (113 ºC). The use of *cis*-LO as a monomer showed a higher conversion level (entry 6; 95%) in line with our previous observation in polycarbonate formation from LO while using an Al(aminotriphenolate) based catalyst.[9c] Despite the higher reactivity of the *cis*-LO, the polymer quality did not improve. The use of cyclohexene-based cyclic anhydride CHE only resulted in the formation of a small oligomer (entry 7; M_n = 2.0 Kg/mol) and low T_g (89 ºC) material. Interestingly, the combination of the rigid naphthoic anhydride NA with CHO (entry 8) provided reasonable molecular weight of poly(CHO-*alt*-NA) at moderate NA conversion (41%) though a promisingly high T_g (140 ºC) could already be attained under these conditions.

Conclusions

In summary, we here describe easily accessible trivalent bifunctional complexes derived from aminotriphenolate ligands and having built-in nucleophiles that, depending on the type of metal, show dynamic coordination behavior. This behavior is a requisite for catalytic activity in the copolymerization of epoxides and cyclic anhydrides, and Cr(III) complex **5** was shown to display the most efficient catalytic features for a small range of epoxide/anhydride combinations. This work thus highlights the use of electronically tunable bifunctional complexes whose catalytic performance can be designed by a proper choice of additives during their formation. Complex **5** shows appreciable activity towards the formation of poly(CHO-*alt*-PA) with a molecular weight of up to 18.4 Kg/mol and a high stiffness as expressed by the observed glass transition (T_g = 144 ºC).

Experimental Section

General Considerations

For details about the general experimental operations and the analytical procedures, please refer to the Supporting Information.

Cyclic Anhydrides, Epoxides and Catalysts

Cyclic anhydride substrates that are commercially available were used after purification by recrystallization from hot $CHCl_3$ in the case of phthalic anhydride, *cis*-1,2,3,6-tetrahydrophthalic anhydride and 1,8-naphtoic anhydride, and dried under vacuum at 40 ºC for 24 h. The commercially available epoxide substrates cyclohexene oxide (CHO) and (*R*)-limonene oxide (LO) were used after distillation over CaH_2. *Cis*-limonene oxide was obtained following a literature procedure[18] and purified by distillation over CaH_2. 4-Dimethylaminopyridine (DMAP) was purified by recrystallization from CH_2Cl_2 and dried under vacuum at 40 ºC for 24 h. The aminotriphenolate ligands **1a**, **1b** and Co complexes **2** and **3** were prepared as described previously[14] and used after drying under vacuum at 40 ºC for 24 h.

Synthesis of Mn complex (4)

To a solution of the aminotriphenolate ligand **1a** (209.5 mg, 0.5 mmol, 1 equiv) in THF (15 mL) was added a solution of $Mn(OAc)_2·6H_2O$ (122.5 mg, 0.5 mmol, 1 equiv) in methanol (10 mL). The mixture was stirred at rt under inert atmosphere. After 18 h the reaction mixture was filtered through Celite and added into a solution of 4-dimethylaminopyridine (DMAP, 171.0 mg, 1.4 mmol, 2.8 equiv) in THF (10 mL). The mixture was stirred in the presence of air at rt for 8 h. Then the solvent was removed to give a brown residue. The resulting compound was recrystallized from THF at rt to give brown crystals suitable for X-ray analysis. Yield: 270.2 mg (0.37mmol, 74 %). ^1H NMR (CD_2Cl_2, 400 MHz, rt): paramagnetic spectrum, δ = 21.30, 14.26, 12.70, 10.46, 3.62, 2.85, 1.75; MALDI(+)-MS (dctb): *m/z* = 593.4 $[M-DMAP]^+$ (calcd. 593.3), 471.4 $[M-2DMAP]^+$ (calcd. 471.2); Anal. calcd. for$C_{41}H_{50}MnN_5O_3·2H_2O$: C 65.50, H 7.24, N 9.31; found: C 65.40, H 7.36, N 9.17. IR (cm^{-1}): 2991, 2907, 2856, 2812, 1608, 1532, 1469, 1433, 1385, 1307, 1259, 1223, 1161, 1070, 1003, 948, 857, 804, 760, 600, 544, 513, 495, 427; UV/vis (CH_2Cl_2, 0.2 mM, 25 ºC; in nm (ε: in $L·mol^{-1}·cm^{-1}$)): 346 (5085), 492 (2205).

Synthesis of Cr complex (5)

A suspension of NaH (57.6 mg, 2.4mmol, 3.3 equiv) in THF (10 mL) was added dropwise into a Schlenk flask containing a solution of aminotriphenolate ligand **1a** (300.0 mg, 0.72 mmol, 1 equiv) in THF (10 mL). The mixture was stirred at rt for 2 h. After this time, anhydrous $CrCl_2$ (1 equiv, 81.3 mg, 0.72mmol) in THF (10 mL) was added. The mixture was stirred at rt for 18 h under an inert atmosphere and then filtered through Celite. Finally, a solution of 4-dimethylaminopyridine (DMAP, 207.0 mg, 1.7 mmol, 2.3 equiv) in THF (10 mL) was added to the flask. The resultant mixture was stirred open to the air at rt for 8 h and then the solvent was removed to give a light purple residue. The resulting chromium complex was further purified by recrystallization using dichloromethane to yield purple crystals suitable for X-ray analysis. Yield: 300.0 mg (0.42mmol, 58 %). ^1H NMR ($CDCl_3$, 400 MHz, rt): paramagnetic spectrum, δ = 16.47, 11.50, 4.22, 3.07, 1.74, 1.16, 0.61; MALDI(+)-MS (dctb): *m/z* = 590.4 $[M-DMAP]^+$ (calcd. 590.3), 468.5 $[M-2DMAP]^+$ (calcd. 468.2); Anal. calcd. for $C_{41}H_{50}CrN_5O_3·1.5H_2O$: C 66.56, H 7.22, N 9.47; found: C 66.54, H 7.60, N 9.45. IR (cm^{-1}): 2987, 2906, 2858, 1613, 1534, 1473, 1439, 1385, 1273, 1224, 1065, 1009, 952, 851, 812, 761, 735, 599, 541, 506, 422 (m); UV/Vis (CH_2Cl_2, 0.2 mM, 25 ºC; in nm (ε: in $L·mol^{-1}·cm^{-1}$): 556 (230).

Synthesis of Co(III) complex (6)

To a solution of the aminotriphenolate ligand **1b** (100.0 mg, 0.186 mmol, 1 equiv) in DCM (15 mL) was added a solution of $Co(OAc)_2 \cdot 4H_2O$ (46.2 mg, 0.186 mmol, 1 equiv) in methanol (10 mL). The mixture was stirred at rt under inert atmosphere for 1 h and then DMAP (68.0 mg, 0.337 mmol) was added causing the color of the mixture gradually changing to red. After 18 h, the reaction mixture was concentrated and the residue recrystallized from acetone/hexane giving **6** as a red solid in 91% yield (142 mg, 0.169 mmol). ^{1}H NMR (CD_2Cl_2, 400 MHz, rt): δ = 8.73 (d, ^3J = 5.0 Hz, 2H, pyr-H), 7.89 (d, ^3J = 5.1 Hz, 2H, pyr-H), 7.09 (s, 1H, ArH), 6.87 (s, 2H, ArH), 6.74 (s, 1H, ArH), 6.67 (d, ^3J = 5.2 Hz, 2H, pyr-H), 6.46 (d, ^3J = 5.0 Hz, 2H, pyr-H), 6.22 (s, 2H, ArH), 4.25 (d, ^2J = 10.8 Hz, 2H, -CH_2N), 3.14 (s, 2H, -CH_2N), 3.12 (s, 6H, NMe_2), 3.02 (d, ^2J not resolved, overlapping signal, 2H, -CH_2N), 3.00 (s, 6H, NMe_2); MALDI(+)-MS (dctb): *m/z* = 1384.7 $[M{-}HNMe_2{+}H]^+$ (calcd. 1384.3); Anal. calcd. for $C_{35}H_{32}CoCl_6N_5O_3 \cdot H_2O \cdot$acetone: C 49.70, H 4.39, N 7.63; found: C 49.23, H 4.41, N 7.46. IR (cm^{-1}): 2900, 1703, 1616, 1537, 1435, 1384, 1364, 1306, 1219, 1173, 1056, 1012, 948, 860, 807, 745, 601, 528, 459. UV/vis (CH_2Cl_2, 0.2 mM, 25 ºC; in nm (ε: in L·mol^{-1}·cm^{-1}): 460 nm (953).

General Procedure for the ROCOP of Cyclic Anhydrides and Epoxides

All reactions were prepared in a glovebox under moisture-free conditions. In a typical experiment, the catalyst (0.05 mmol), co-catalyst/nucleophile (0.025 mmol) and 4.0 mmol of the cyclic anhydride were added into the Schlenk tube with a Teflon stirring bar. Then, the epoxide (4.4 mmol, 1.1 equiv.) and solvent (THF, 0.50 mL) were added and the tube was closed with a glass cap. The reaction mixture was stirred at the desired reaction temperature. The reaction mixture was monitored by ^{1}H NMR ($CDCl_3$) and when no further anhydride could be observed, all volatiles were removed under vacuum. The crude reaction mixture was analyzed by ^{1}H NMR spectroscopy to determine the conversion to polymer and the amount of ether linkages. The crude reaction was dissolved in a minimum amount of CH_2Cl_2 and the polymer precipitated by addition of a 1 M solution of HCl in MeOH (this step was repeated two times). Upon settling, the supernatant solution was decanted and discarded. Then, the polymer was washed with a solution of methanol. Finally, the purified polymer was dried under vacuum at 40°C for 24 h and analyzed by ^{1}H, $^{13}C\{^1H\}$ NMR, IR, DSC, TGA and GPC. See Supporting Information for more details.

Crystallographic analysis

General procedure: The measured crystals of **4–6** were stable under atmospheric conditions; nevertheless, it was treated under inert conditions immersed in perfluoro-polyether as protecting oil for manipulation. Data Collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX II 4K CCD area detector, a FR591 rotating anode with Mo Kα radiation, Montel mirrors and a Kryoflex low temperature device (T = −173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008−1 (2008). Structure Solution: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[19] Structure Refinement: SHELXTL-97-UNIX VERSION. Details for complex **4** and the NaOAc-ligated dimeric complex $[\mathbf{6}]_2 \cdot 2NaOAc \cdot (acetone)_2$are provided in the Supporting Information and CCDC-1819099 and 1819097, respectively.

Crystal data for Cr-complex **5**: $C_{43.25}H_{54.5}Cl_{4.5}CrN_5O_3$, M_r = 903.94, triclinic, *P*-1, a = 17.006(2) Å, b = 17.1256(19) Å, c = 18.217(3) Å, α = 80.087(4)º, β = 83.373(4)º, γ = 60.563(4)º, V = 4548.7(10) Å^3, Z = 4, ρ = 1.320 mg·M^{-3}, μ = 0.559 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 1894, crystal size = 0.35 × 0.10 × 0.04 mm, θ(min) = 1.135°, θ(max) = 25.487°, 25395 reflections collected, 16493 reflections unique (R_{int} = 0.0793), GoF = 1.041, R_1 = 0.0744 and wR_2 = 0.2046 [$I > 2\sigma(I)$], R_1 = 0.0982 and wR_2 = 0.2196(all indices), min/max residual density = −1.178/1.019 [e·Å^{-3}]. Completeness to θ(25.487°) = 97.5%. CCDC number 1819100.

Crystal data for Co-complex **6**: $C_{41}H_{44}Cl_6CoN_5O_3$, M_r = 958.44, monoclinic, *P*2(1)/n, a = 8.7128(13) Å, b = 18.614(3) Å, c = 26.949(4) Å, α = 90º, β = 93.899(6)º, γ = 90º, V = 4360.4(11) Å^3, Z = 4, ρ = 1.460 mg·M^{-3}, μ = 0.811 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 1976, crystal size = 0.12 × 0.08 × 0.01 mm, θ(min) = 1.896°, θ(max) = 25.018°, 35826 reflections collected, 7664 reflections unique (R_{int} = 0.1378), GoF = 0.987, R_1 = 0.0603 and wR_2 = 0.1172 [$I > 2\sigma(I)$], R_1 = 0.1345 and wR_2 = 0.1406 (all indices), min/max residual density = −0.480/0.614 [e·Å^{-3}]. Completeness to θ(25.018°) = 99.6%. CCDC number 1819098.

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Keywords: aminotriphenolate ligands • bifunctional catalysis • cyclic anhydrides • epoxides • polyesters

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[15] The X-ray molecular structures determined for **4** and **5** are rather similar and therefore only the crystal structure of the Cr-complex is shown in Figure 2, see Supporting Information for further details.

[16] During the isolation and crystallization of Co-complex **6**, we found other types of crystals that were analyzed as a DMAP-free assembly of two Co(III)aminotriphenolates that are held together via two molecules of NaOAc. The latter likely originates from the first step of the preparation, see Supporting Information for details.

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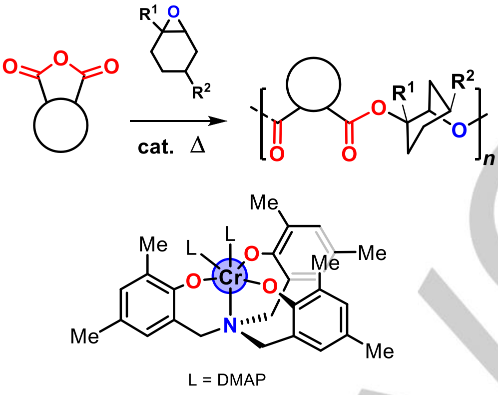
Entry for the Table of Contents:

FULL PAPER

New bifunctional aminotriphenolate complexes (M = Mn, Co, Cr) have been prepared and used as catalysts for the ring opening polymerization of cyclic anhydrides and epoxides. The Cr(III)-based complex showed the best catalytic performance providing high molecular weight rigid polyesters with M_n values of up to 18.4 Kg/mol and glass transition temperatures up to 144 ºC in the case of poly(cyclohexene oxide-*alt*-phthalic anhydride).



Polyesters*

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Bifunctional Aminotriphenolate Complexes as One-Component Catalysts for the ROCOP of Cyclic Anhydrides and Epoxides

*one or two words that highlight the emphasis of the paper or the field of the study