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Anaerobic Solid-phase Thermal Tetrahedral-to-Octahedral Transformation of Some Cobalt (II) complexes

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Abstract

New examples of thermal tetrahedral-to-octahedral transformation were observed and studied by the thermal reactions of disodium tetrakis(aryloxo)cobaltate(II) complexes, $Na_2[Co(OAr)_4(THF)_m](THF)_n$ [OAr = *o*-chloro-, *o*-bromo-, *m*-chloro-, *p*-bromo-, *2,4*-dichloro-, *2,4*-dimethyl- or *2,6*-dichlorophenoxide; m = 2 (m = 0 for 2,4-dimethylphenoxide complex; n = 1-3) in the solid phase. With one exception, the original complexes were all violet and have octahedral configurations. The exception was $Na_2[Co(2,4\text{-}(Me)_2C_6H_3O)_4]$.THF, which has an intense blue color and its electronic and magnetic data were characteristic for tetrahedral cobalt(II) complexes. The aryloxide complexes of *2,6*-dichloro-, *m*-chloro-, and *p*-bromophenoxide showed a two-step thermochromism (violet→blue→rose) upon heating. These steps may be due to the structure changes to tetrahedral THF-free complexes and then to an aryloxide bridged polymers containing octahedral cobalt(II) ions. The complexes of *o*-Chloro- and *o*-bromophenoxide were underwent to thermal desolvation-polymerization in one step, changing directly into the rose aryloxide bridged polymers. The complex of 2,4-DichSorophenoxide showed only one-step thermochromism (violet→blue), thus changing from octahedral to tetrahedral configuration. Whereas the complex of *2,4*-Dimethylphenoxide did not show any color change and retained its tetrahedral structure till decomposition. The reverse changes of the thermal products proceeded on standing under dry THF atmosphere, for some hours or days.

Keywords: Thermal transformation, Cobalt(II) complexes, Thermochromism, Desolvation, Polymerization.

Introduction

In addition to the thermochromic phenomena observed in solutions, numerous changes are also known to occur in the solid-state among the transition metal complexes, such complexes show that their configurations can be readily converted into different ones by changing their chemical and physical environments. This structural lability implies that the energy gap between instance structural stereoisomers is small which are usually encountered in many Ni(II) and Cr(III) complexes [1-11]. In these complexes, a small differences in the electronic properties and steric requirements of the tigands are reflected in the structure that they prefer when heated then cooled [3-11]. Most of the often observed solid-phase thermal transformation of transition metal complexes are the octahedral-to-tetrahedral or octahedral-to-square planar transformation, in which a part of the ligand (i.e., H_2O) is lost on heating so that the change is not isomeric. On the other hand, the thermal tetrahedral-to-octahedral isomeric transformation was not often observed [3-12]. In the present work, we have found new examples of this type of transformation in the thermal reaction of disodium tetrakis(aryloxide)-cobaltate(ll) complexes. In these complexes, *two* effects, due to the substituent groups on the pheuoxide ring, seem to influence the modes of their thermal reactions, their inductive effect and steric hinderance. In this paper, thermal reactions of these complexes in the solid-phase were investigated.

2. Materials and methods

2.1. Instrumentation

Infrared spectral measurements for the free ligand and its metal complexes were recorded in Nujol mulls or CsI pellets using a Perkin-Elmer 598 spectrometer. Nujol mulls using a Perkin-Elmer 550 spectrophotometer. Magnetic moments were measured by Gouy's method at room temperature. Thermal analyses of the complexes were recorded on Perkin-Elmer high temperature differential thermal analyser, Delta series TGA , with 3700 Data station in the atmosphere of nitrogen. The temperature scale of the instrument was calibrated with high purity calcium oxalate. Accurately 5 mg of pure sample was subjected for dynamic TG scans at heating rate of 10 °C min^{-1}. Due to the high air-sensitivity of the complexes under investigation, various experimental manipulations were performed under stringent precautions to avoid moisture and atmospheric oxygen. All thermal reactions and subsequent handling of materials were carried out under argon using Schlenk techniques [18]. The preparation of the original complexes has been previously described [13].

2.2. Visual observations of thermochromic changes

In order to study the thermal reactions of the complexes under investigation and the mode of thermochromic colour change of each complex, which usually occurs within a temperature range of several degrees, a sample of the complex under investigation is heated slowly to determine: first, the temperatures at which distinct colour changes will be observed. Second, for each observable color change, a new sample is heated to the temperature at which this color took place (see A and B).

A: For the blue products (first-step thermochromism)

In a two-neck Schlenk tube provided with a thermometer and an in- and out-let device for argon, a small amount of finely powdered sample of a given complex was heated slowly in a silicon oil bath. The heating rate did not exceed 5° C/min. The heating was continued until the first distinct colour change was observed. At this temperature the sample was left to stand for further 1/2 hr, to ensure the removal of all liberated THF and to avoid the occurance of a backward reaction towards the original complex. The new product was allowed to cool under argon to room temperature and then identified and finally stored under argon.

B: For the rose products (second-step thermochromism)

A new sample was heated to the temperature at which the rose product was formed and then treated as above. The rose product could be also obtained by further heating of the blue product obtained in (A), but it was preferable to obtain the rose product from a new sample.

3. Results and discussion

3.1. Characterization of the solid complexes

The preparations of the solid complexes and their properties in solution have been described previously [13]. Analytical, spectral and magnetic moments data of the complexes, summarized in Table 1, lead to the formulae given, and show that all the complexes, except the 2,4-dimethylphenoxide complex have high-spin octahedral configurations.

The observed spectral bands and their positions, indicate clearly that the original complex has an octahedral structure [14]. The spectra of the other complexes are similar and also indicate their octahedral structures. The 2,4-dimethylphenoxide complex, $Na_2[Co(OAr)_4]$.THF, is intense blue colored and has a tetrahedral configuration.

3.2. Spectral and magnetic changes of the complexes

Figure 1 shows a comparison of the electronic spectra of both the obtained blue and rose species of the 2,6-dichlorophenoxide complex with the spectrum of the original violet complex. The spectrum of the blue product shows obvious spectral changes and a broad band appears with higher intensity characteristic to tetrahedral Co(II) complexes [14] (Table 1). The rose product has a spectral pattern similar to that of the original violet octahedral species except for a slight shift of the bands, which indicates partial exchange of the ligands achieved through the formation of an aryloxide bridged polymer [14,15]. The spectra of the rose products of o-chloro and o-bromophenoxide complexes are shown in Figure 2. The complexes have spectral patterns identical with those of the original violet Complexes. The spectra of the obtained blue products of 2,4-dimethyl and 2,4-dichlorophenoxide complexes (for 2,4-dimethyl complex, the measured spectrum was for a blue species obtained at a higher temperature than those at which the other blue products were formed) are shown in Figures 3 and 4. In the former case, the spectral pattern remains nearly unchanged after the liberation of the crystallized THF, showing that the tetrahedral configuration of this complex is retained. In the latter case, however, there is an obvious spectral changes and bands characteristic to tetrahedral Configuration appear [14].

Table 1: Analytical analyses, electronic spectra and magnetic moments of the original complexes

Complex		Found(Calc.)			Absorption maxima, 10^{-3} cm^{-1}			μ_{eff} (BM
	Color	Co%	Na%	OAr%				
$Na_2[Co(2,6\text{-}Cl_2C_6H_{30})_4(THF)_2]\cdot 2THF$	violet	5.8(5.7)	4.5(4.4)	60.9(62.2)	18.00	18.80	19.40	5.43
$Na_2[Co(2,6\text{-}Cl_2C_6H_3O)_4]$	blue	8.2(7.8)	6.3(6.1)	84.7(84.1)	16.80	17.50(sh)	18.20(sh)	4.61
$\{Na_2[Co(2,6\text{-}Cl_2C_6H_3O)_4]\}_n$	rose	7.7(7.8)	6.4(6.1)	84.3(84.1)	18.00	18.60	--	5.15
$Na_2[Co(2,4\text{-}$	violet	6.3(6.1)	4.6(4.7)	66.6(66.9)	18.80	19.20(sh)	20.00	5.32
$Na_2[Co(2,4\text{-}Cl_2C_6H_3O)_4]$	blue	7.8(7.8)	6.0(6.1)	85.7(86.1)	16.60	17.30(sh)	17.80(sh)	4.65
$Na_2[Co(2,4\text{-}(Me)_2C_6H_3O)_4]\cdot THF$	blue	9.6(9.0)	6.8(7.0)	73.6(73.2)	16.90	17.90	18.10	4.47
$Na_2[Co(2,4\text{-}(Me)_2C_6H_30)_4]$	blue	9.9(10.0)	7.6(7.8)	82.6(82.2)	16.70	17.40	18.00	4.43
$Na_2[Co(o\text{-}ClC_6H_4O)_4(THF)_2]\cdot 3THF$	violet	6.2(6.0)	4.5(4.7)	52.7(52.3)	18.50	19.40	19.80	5.2-8
$\{Na_2[Co(o\text{-}ClC_6H_4O)_4\}_n$	rose	9.0(9.6)	7.1(7.5)	83.7(83.0)	18.40	19.20(sh)	19.60	5.17
$Na_2[Co(m\text{-}ClC_6H_4O)_4(THF)_2]\cdot 2THF$	violet	5.4(5.5)	5.0(5.1)	57.6(56.5)	18.70	19.80	20.10	5.22
$Na_2[Co(m\text{-}ClC_6H_4O)_4]$	blue	9.8(9.6)	7.3(7.5)	83.9(83.0)	17.05	17.60(sh)	18.20(sh)	4.58
$\{Na_2[Co(m\text{-}ClC_6H_4O)_4]\}_n$	rose	9.3(9.6)	7.4(7.5)	82.3(83.0)	19.20	19.10	19.85	5.11
$Na_2[Co(o\text{-}BrC_6H_4O)_4(THF)_2]\cdot 2THF$	violet	5.5(5.5)	4.1(4.3)	64.0(63.6)	18.60	19.20	19.50	5.18
$\{Na_2[Co(o\text{-}BrC_6H_4O)_4]\}_n$	rose	7.3(7.4)	6fO(5.8)	85.3(86.8)	18.90	19.20	19.70	5.07
$Na_2[Co(p\text{-}BrC_6H_4O)_4(THF)_2]\cdot 3THF$	violet	5.2(5.1)	3.8(4.0)	58.2(59.1)	19.10	19.45	19.60	5.12
$Na_2[Co(o\text{-}BrC_6H_4O)_4]$	blue	7.7(7.4)	6.3(5.8)	86.1(86.8)	17.25	18.40(sh)	18.90(sh)	4.45
$\{Na_2[Co\text{-}(p\text{-}BrC_6H_4O)_4\}_n$	rose	7.1(7.4)	5.4(5.8)	87.1(86.8)	19.20	19.55	19.75	5.03

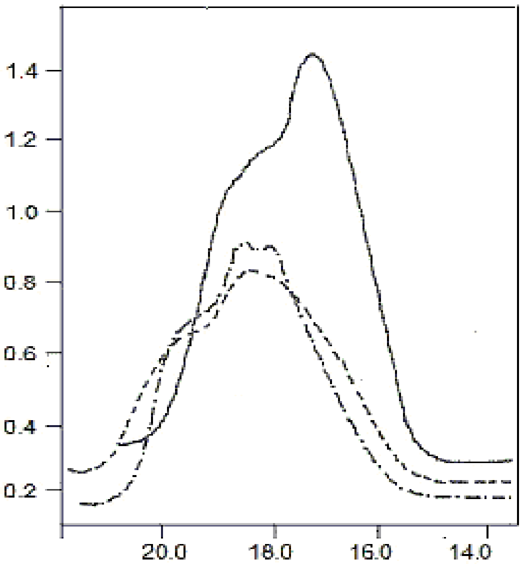

Figure 1. Electronic spectra of complex $Na_2[Co(2,6\text{-}Cl_2C_6H_3O)_4(THF)_2]\cdot 2THF$ (-.-.-) and its thermal products: blue (—) and rose (-----).

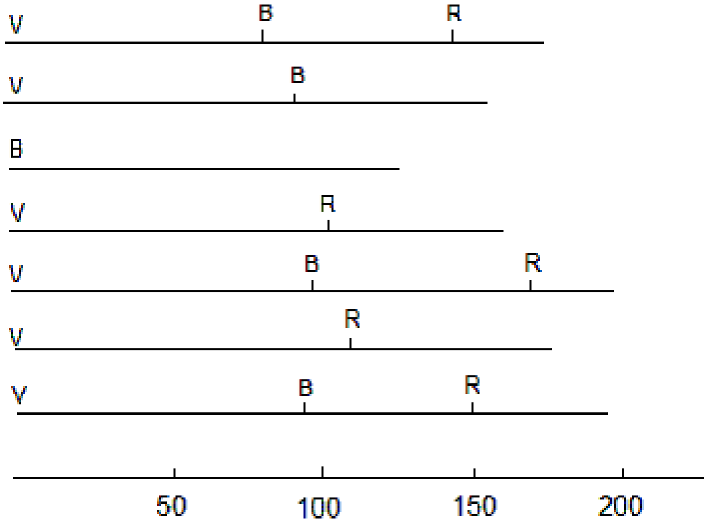

Figure 2. Results of visual observations on the thermochromic changes of the complexes. V: violet; B: blue; R: rose. The high temperature colors are shown at the spots on the temperature scale (horizontal) where they begin to appear

The magnetic susceptibilities for the obtained thermal products are given in Table 1. The data shows obvious changes in the moments of the blue tetrahedral products obtained by heating the original complexes corresponding to configurationally changes from octahedral to tetrahedral structures. The magnetic moments of the rose products indicate their octahedral configurations. The lowering (-5%) in the μ values of the rose products compared to those of the original violet complexes is attributed to the antiferromagnetic interactions between Co(TI) ions in the octahedral aryloxide bridged polymer.

3. 3. Infrared spectra

All complexes show the characteristic ν(CO) of the aromatic ring at 1500 cm^{-1}. The spectra of the thermal products (blue and rose) show the absence of the observed band at 1050 cm^{-1} in the spectra of the original complexes assigned [16] to ν(C-O-C) of the THF molecules which reflects the liberation of the THF molecules upon heating. On the other hand, the ν(Co-O) appears in the spectra of the rose products at lower frequency of ~ 450 cm^{-1} than its value in the case of the blue or violet complexes (~ 490 cm^{-1}). The shift of 40 cm^{-1} in ν(Co-O) [16,17], indicates the polymeric structure of the rose products as confirmed by the values of its magnetic moments. In the case of tetrahedral complexes, a very broad band is observed at 3580 cm^{-1} and is assigned to the spin allowed $^4A_2 \rightarrow ^4T_2$ transition of Co(II) ions [14]. The thermal reactions of the complexes under study are accompanied by distinct color or structural changes can be classified into the following three types:

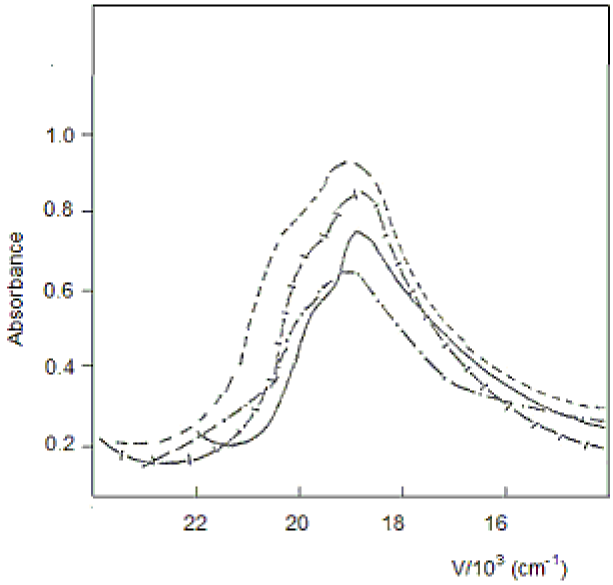

Figure 3. Electronic spectra of the original o-chloro (—) and o-bromo (-I-I-I-)) complexes and their thermal products (———) and (-·-·-·-·), respectively.

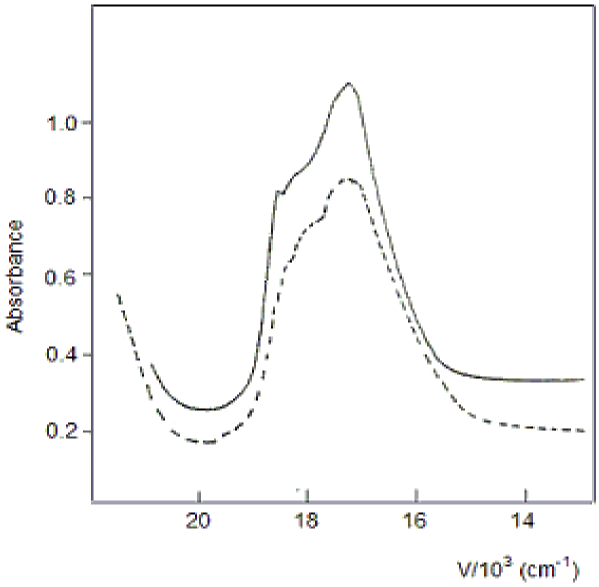

Figure 4. Electronic spectra of the original 2,4-dimetyl complex (–) and its thermal product (----).

(a) $Na_2[Co(OAr)_4(THF)_2]$ (Oh) $\xrightarrow[\Delta]{-2THF}$ $-[-Na_2[Co(OAr)_4-]_n-$ (Oh')

(b) $Na_2[Co(OAr)_4(THF)_2]$ (Oh) $\xrightarrow[\Delta]{-2THF}$ $Na_2[Co(OAr)_4]$ (T_h) $\xrightarrow{\Delta}$ $-[-Na_2[Co(OAr)_4-]_n-$ (Oh')

(c) $Na_2[Co(OAr)_4(THF)_2]$ (Oh) $\xrightarrow[\Delta]{-2THF}$ $Na_2[Co(OAr)_4]$ (T_h)

Where, ($O_{h)}$ and (O_h') represent monomeric, polymeric octahedral species and (T_h) represents the resolved tetrahedral ones. The mode of thermal reactions thus seems to depend on more complicated structure factors. In the case of phenoxide complexes, the steric hinderance of the two methyl groups seem to play the main role for retaining its tetrahedral configuration.

3.4. Thermochromism of the complexes

Figure 5 shows the results of visual observations on the solid-phase thermochromism of the complexes. All complexes, except 2,4-dimethylphenoxide complex, change their colour from violet to blue or from violet to rose as a first-step thermochromism at a relatively low temperature (ca. 128° C or lower). The changes observed in 2,6-dichloro-, m-chloro- and p-bromophenoxide complexes are especially remarkable since they show a second colour change from blue to rose upon continued healing, leading to a two-step thermochromism (violet →blue→rose). o-Chloro- and o-bromo-phenoxide complexes "change their colour directly to rose" in one-step thermochromism. On the other hand, 2,4-dichlorophenoxide complex shows only one-step thermochromism, from violet to blue, whereas the remainder 2,4-dimethylphenoxide complex does aot show any colour changes until it decomposed. All transformations proceeded endothermically and the thermal products could be isolated and identified at room temperature and under anaerobic conditions. The reverse changes of the thermal products proceed on standing under dry THE atmosphere, but so slowly that it takes some hours or days to return completely to the original violet complexes. The rose product of 2,6-dichlorophenoxide complex retains its parent color in much more time (8 days) rather than those of m-chloro- or g-bromophenoxide complexes (6 days for each). On the other hand, the rose products of o-chloro- and o-bromophenoxide complexes revert to the original violet complexes after 12-15 days. The blue products of the complexes also revert to the original complexes more or less gradually.

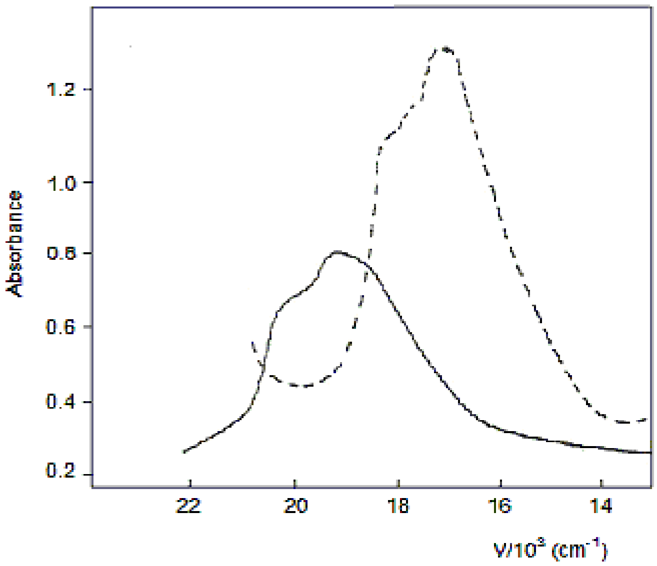

Figure 5. Electronic spectra of the original 2,4-dichloro complex (–) and its thermal blue thermal product (----).

3.5. Thermal analyses

The results of TG-DTA analyses of 2,6-dichloro, *m*-chloro- and p-bromophenoxide complexes are shown in Table 2.

Table 2: Thermal analysis of the metal complexes

Complex	Desolvation		Th→Oh	ransformation
	Temp./^{o}C	%Wt loss, Found(Calc.)	Temp./^{o}C	ΔH/kJmol^{-1}
$Na_2[Co(2.6\text{-}Cl_2C_6H_3O)_4(THF)_2]\cdot 2THF$	54-74 85-98	13.69(13.83)	150-162	6.95
$Na_2[\ Co(2,4\text{-}Cl_2C_6H_3O)_4(THF)_2]\cdot THF$	53-66 95-108	6.98(7.43) 21.89(22.29)		
$Na_2[Co(2,4\text{-}(Me)_2C_6H_3O)_4]\cdot THF$	56-72	10.33(10.88)		
$Na_2[Co(o\text{-}ClC_6H_4O)_4(THF)_2]\cdot 3THF$	48-65 105-116	21.85(22.14) 36.29(36.90)		
$Na_2[Co(m\text{-}ClC_6H_4O)_4(THF)_2]\cdot 2THF$	55.71 100-120	15.37(15.95) 31.45(31.88)	172-188	23.80
$Na_2[Co(o\text{-}BrC_6H_4O)_4(THF)_2]\cdot 2THF$	49-68 113-128	12.89(13.32) 25.98(26.64)		
$Na_2[Co(p\text{-}BrC_6H_4O)_4(THF)_2]\cdot 3THF$	58-70 95-107	21.23(20.52) 33.75(34.20)	149-163	7.68

The TG curves show two abrupt weight losses. The first weight loss observed before 85° C, and the corresponding endothermic DTA peaks, are due to the liberation of the crystallized THF molecules of crystallization (2, 2 and 3 moles, respectively). The second weight loss and the corresponding endothermic DTA peaks are due to the splitting of two moles of coordinated THF which are responsible for the first color change (violet→blue). On the other hand, the endothermic peaks at 156 °C for 2,6-dichloro, 179° C for m-chloro- and 158° C for *p*-bromophenoxide complexes apparently correspond to the second color change, from blue to rose, in which the TG curves remain flat. The results of TG-DTA analyses of 2,4-dichloro and 2,4-dimethylpheno- oxide complexes. The DTA curve of the former gives two endothermic peaks corresponding to the two abrupt weight losses as observed in the TG curve. The first peak, at 59° C, is due to liberation of one mole of THF, whereas the second peak, at 100° C, is due to splitting of the two coordinated THF molecules, which is at the same time, corresponding to the color change from violet to blue. The DTA curve of the latter complex shows only one endothermic peak at 68° C, which is due to the liberation of one mole of THF of crystallization, as judged from the abrupt weight loss observed in the TG curve. Both curves give no further endothermic peaks until the complexes decompose on strong heating.

Conclusion

New examples of thermal tetrahedral-to-octahedral transformation were observed and studied by the thermal reactions of disodium-tetrakis(aryloxo)cobaltate(II) complexes, $Na_2[Co(OAr)_4(THF)_m](THF)_n$ [OAr = o-chloro-, o-bromo-, m-chloro-, fi-bromo-, 2,4-dichloro-, 2,4-dimethyl- or 2,6-dichlorophenoxide; m = 2 (m = 0 for 2,4-dimethylphenoxide complex; n = 1-3) in the solid phase. With one exception, the original complexes were all violet and have octahedral configurations. The exception was $Na_2[Co(2,4\text{-}(Me)_2C_6H_3O)_4]$.THF, which has an intense blue color and its electronic and magnetic data were characteristic for tetrahedral cobalt(II) complexes. The aryloxide complexes of 2,6-dichloro-, m-chloro-, and p-bromophenoxide showed a two-step thermochromism (violet→blue→rose) upon heating. These steps may be due to the structure changes to tetrahedral THF-free complexes and then to an aryloxide bridged polymers containing octahedral cobalt(II) ions. The complexes of o-Chloro- and o-bromophenoxide were underwent to thermal desolvation-polymerizationin in one step, changing directly into the rose aryloxide bridged polymers. The complex of 2,4-DichSorophenoxide showed only one-step thermochromism (violet→blue), thus changing from octahedral to tetrahedral configuration. Whereas the complex of 2,4-Dimethylphenoxide did not show any color change and retained its tetrahedral structure till decomposition. The reverse changes of the thermal products proceeded on standing under dry THF atmosphere, for some hours or days.

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