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Anaerobic Solid-Phase Thermal Configurational Transformations of Cobalt(II) Complexes

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New examples of thermal tetrahedral-to-octahedral transformation were discovered and studied in the thermal reactions of disodium tetrakis(aryloxo)cobaltate(II) complexes, of the formula $Na_2[Co(OAr)_4(thf)_m]\cdot n$thf (OAr = *o* − chloro − , *o*-bromo-, *m*-chloro-, *p*-bromo-, 2,4-dichloro-, 2,4-dimethyl- or 2,6-dichlorophenoxo; $m = 2$ for all complexes except for 2,4-dimethylphenoxo complex where $m = 0$; thf: tetrahydrofuran; $n = 1$—3), in the solid phase. With one exception, the original complexes were all violet colored and have octahedral configurations. The exception is $Na_2[Co(2,4\text{-}Me_2C_6H_3O)_4]\cdot$thf, which has an intense blue color and its electronic and magnetic data are characteristic of tetrahedral cobalt(II). The aryloxo complexes of 2,6-dichloro-, *m*-chloro-, and *p*-bromophenoxo show a two-step thermochromism, violet→blue→rose, upon heating. These steps correspond to structural changes to tetrahedral thf-free complexes and then to aryloxo bridged polymers with octahedral cobalt(II) ions, respectively. *o*-Chloro- and *o*-bromophenoxo complexes underwent only thermal desolvation–polymerization, which occurs in one step, changing directly into the rose aryloxo-bridged polymers. 2,4-Dichlorophenoxo complex shows only one-step thermochromism, violet→blue, thus changing from the octahedral to tetrahedral configuration. The remainder complex, of 2,4-dimethylphenoxo, does not show any color changes and retained its tetrahedral configuration until it decomposed. The reverse changes of the thermal products to the original complexes proceed on standing under dry thf atmosphere, for some hours or days.

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, which show the peculiarity that their configurations can be readily converted into different ones by a change in their chemical and physical environments. This structural lability implies that the energy gap between different structural stereoisomers is small, which are usually encountered in many Ni(II) and Cr(III) complexes.[1—11] In these complexes, small differences in the electronic properties and steric requirements of the ligand 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 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] Recently, we have found new examples of this type of transformation in the thermal reaction of disodium tetrakis(aryloxo)cobaltate(II) complexes. In these complexes, two effects, due to the substituent groups on the phenoxo ring, seem to influence the modes of their thermal reactions, one is their inductive effect, the other is their steric hinderance. In this paper, thermal reactions of these complexes, in the solid-phase, were investigated.

Experimental

Due to the high air-sensitivity of the complexes under investigation, various experimental manipulations were done with stringent precautions to avoid moisture and atmospheric oxygen. All thermal reactions and subsequent handling of materials were done under argon using Schlenk techniques.[13] The preparation of the original complexes has been described.[14] The elemental analyses were done on samples loaded and weighed under an argon atmosphere using special weighing tubes provided with a thin-walled glass bulb; once the sample was weighed, the glass bulb was broken in a beaker and the analyses were then done.

Visual Observations of Thermochromic Changes. To study the thermal reactions of the complexes under investigation and the mode of thermochromic color change of each complex, which usually occurs within a temperature range of several degrees, a sample of the complex under investigation was heated slowly to identify, first, the temperatures at which distinct color changes are observed. For each observable color change, a new sample was heated to the temperature at which this color change took place (see A and B).

[A] For the Blue Products (First-Step Thermochromism). In a two-neck Schlenk tube provided with a thermometer (mercury thermoregulator coupled with controller) 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^{-1}. The heating was continued until the first distinct color change was observed. At this temperature the sample was left to stand for a further 1/2 h, 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. Elemental analyses are given in Table 1.

[B] For the Rose Products (Second-Step Thermochromism). A new sample was heated to the temperature at which the rose prod-

Table 1. Elemental Analyses, Electronic Spectra, and Magnetic Moments of the Original Complexes[a)] and the Resulted Thermal Products

Complex	Color	Analytical data (%)[b)]			Absorption maxima			μ_{eff}
		Co	Na	OAr	$\nu\ 10^{-3}/\mathrm{cm}^{-1}$			B.M.
$Na_2[Co(2,6\text{–}Cl_2C_6H_3O)_4(thf)_2]\cdot 2thf$[a)]	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
$\text{–}[\text{–}Na_2[Co(2,6\text{–}Cl_2C_6H_3O)_4]\text{–}]_n\text{–}$	Rose	7.7 (7.8)	6.4 (6.1)	84.3 (84.1)	18.00	18.60	—	5.15
$Na_2[Co(2,4\text{–}Cl_2C_6H_3O)_4(thf)_2]\cdot thf$[a)]	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
$Na_2[Co(2,4\text{–}Me_2C_6H_3O)_4]\cdot(thf)$[a)]	Blue	9.6 (9.0)	6.8 (7.0)	73.6 (73.2)	16.90	17.90	18.10	4.47
$Na_2[Co(2,4\text{–}Me_2C_6H_3O)_4]$	Blue	9.9 (10.0)	7.6 (7.8)	82.6 (82.2)	16.70	17.40	18.00	4.43
$Na_2[Co(o\text{–}ClC_6H_4O)_4(thf)_2]\cdot 3thf$[a)]	Violet	6.2 (6.0)	4.5 (4.7)	52.7 (52.3)	18.50	19.40	19.80	5.28
$\text{–}[\text{–}Na_2[Co(o\text{–}ClC_6H_4O)_4\text{–}]_n\text{–}$	Rose	9.0 (9.6)	7.1 (7.5)	83.7 (83.0)	18.40	19.20 (sh)	19.60	5.17
$Na_2[Co(m\text{–}ClC_6H_4O)_4(thf)_2]\cdot 2thf$[a)]	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
$\text{–}[\text{–}Na_2[Co(m\text{–}ClC_6H_4O)_4]\text{–}]_n\text{–}$	Rose	9.3 (9.6)	7.4 (7.5)	82.3 (83.0)	19.20	19.10	19.85	5.11
$Na_2[Co(o\text{–}BrC_6H_4O)_4(thf)_2]\cdot 2thf$[a)]	Violet	5.5 (5.5)	4.1 (4.3)	64.0 (63.6)	18.60	19.20	19.50	5.18
$\text{–}[\text{–}Na_2[Co(o\text{–}BrC_6H_4O)_4]\text{–}]_n\text{–}$	Rose	7.3 (7.4)	6.0 (5.8)	85.3 (86.8)	18.90	19.20	19.70	5.07
$Na_2[Co(p\text{–}BrC_6H_4O)_4(thf)_2]\cdot 3thf$[a)]	Violet	5.2 (5.1)	3.8 (4.0)	58.2 (59.1)	19.10	19.45	19.60	5.12
$Na_2[Co(p\text{–}BrC_6H_4O)_4]$	Blue	7.7 (7.4)	6.3 (5.8)	86.1 (86.8)	17.25	18.40 (sh)	18.90 (sh)	4.45
$\text{–}[\text{–}Na_2[Co(p\text{–}BrC_6H_4O)_4\text{–}]_n\text{–}$	Rose	7.1 (7.4)	5.4 (5.8)	87.1 (86.8)	19.20	19.55	19.75	5.03

b) Found (Calcd).

uct 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. Elemental analyses are given in Table 1.

Measurements. Sodium was analyzed using a PEP7 flame photometer. Cobalt was measured by a complexometric method.[15)] Aryloxo anions were measured by acid/base titration and potentiometric titration. TG-DTG and TG-DSC measurements were done using a Perkins–Elmer high temperature differential thermal analyser, Delta series TGA, with 3700 Data station. The conditions of the runs are given in the captions of the figures. Electronic spectra for the solid-phase were measured as Nujol mulls using a Perkins–Elmer 550 spectrophotometer. Infrared spectra were recorded as Nujol mulls or CsI pellets; using a Perkins–Elmer 598 spectrophotometer. Magnetic measurements were made with a Gouy balance of standard design. A standard double Dewar served for low temperature measurements. Mass spectra were recorded on a Hewlett–Packard mass spectrometer, model MS 5988.

Results and Discussion

Structure of the Original Solid Complexes. The preparation of the solid complexes and their properties in solutions have been described previousely.[14)] The complexes are violet colored. Analytical, spectral, and magnetic moments data of the complexes, Table 1, (spectral and magnetic moments data were not previously reported), lead to the formulae given, and show that all the complexes, except the 2,4-dimethylphenoxo complex, have high-spin octahedral configurations. The spectrum of one of them, 2,6-dichlorophenoxo complex (together with those of its thermal reaction products: see latter) is shown in Fig. 1. The observed bands and their positions clearly indicate that the original complex has an octahedral structure.[16)] The spectra of the other octahedral complexes are similar. The 2,4-dimethylphenoxo complex, $Na_2[Co(2,4\text{-}Me_2C_6H_3O)_4]\cdot thf$, is intensely blue colored and has a tetrahedral configuration as judged by its magnetic and spectral data.

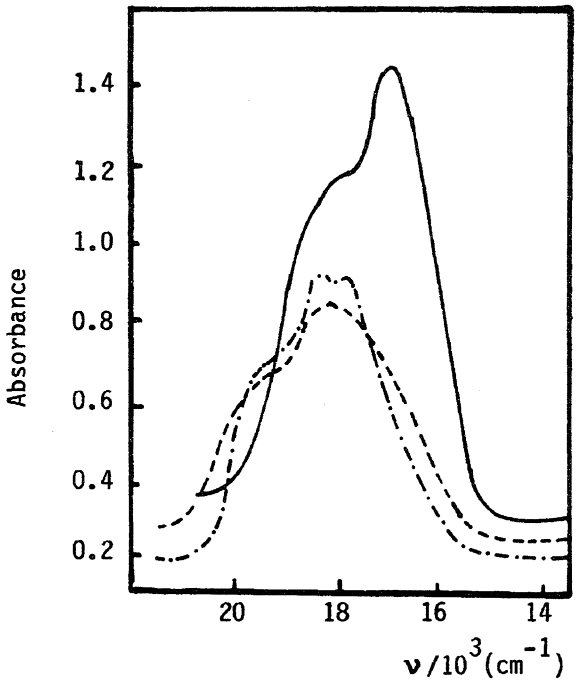

Fig. 1. Electronic spectra of the $Na_2[Co(2,6\text{-}Cl_2C_6H_3O)_4(thf)_2]\cdot 2thf$ complex (–••–) and its thermal products; blue (——) and rose (- - -).

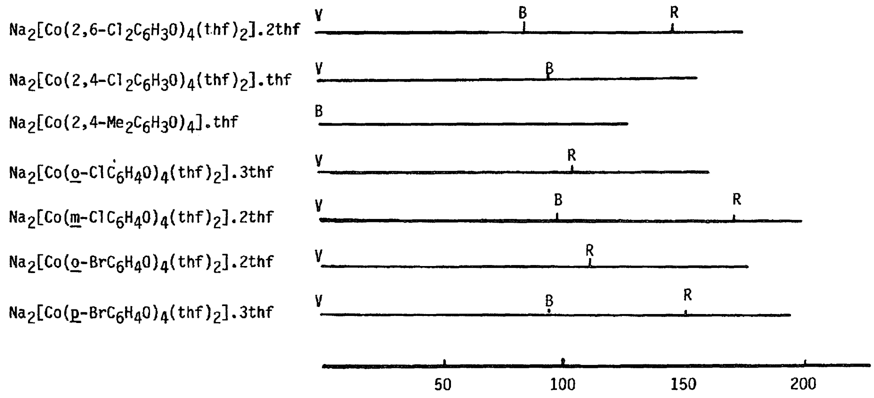

Fig. 2. Results of visual observations on the thermochromic changes of the complexes. V: violet, B: blue, R: rose. The high-temperature colours are shown at the spots on the temperature scale (horizontal) where they begin to appear.

Thermochromism of the Complexes. Figure 2 shows the results of visual observations on the solid-phase thermochromism of the complexes. All the complexes, except 2,4-dimethylphenoxo complex, change their colors from violet to blue or from violet to rose at a relatively low temperature (about 128 °C or lower) as a first-step thermochromism. The changes observed in 2,6-dichloro-, *m*-chloro-, and *p*-bromophenoxo complexes are especially remarkable since they show a second color change from blue to rose upon continued heating, leading to a two-step thermochromism (violet→blue→rose). *o*-Chloro- and *o*-bromophenoxo complexes change their color directly to rose in one-step thermochromism. On the other hand, 2,4-dichlorophenoxo complex shows only one-step thermochromism, from violet to blue, while the remaining 2,4-dimethylphenoxo complex does not show any color 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 proceeded on standing under a dry thf atmosphere, but so slowly that it took some hours or days to return completely to the original violet complexes. Thus, the rose product of 2,6-dichlorophenoxo complex retained its parent color for much more time (8 d) than those of *m*-chloro- or *p*-bromophenoxo complexes (6 d for each). However, the rose products of *o*-chloro- and *o*-bromophenoxo complexes reverted to the original violet complexes after 12—15 d. The blue products of the complexes also reverted to the original complexes more or less gradually.

Thermal Analyses. The results of TG-DTA analyses of 2,6-dichloro, *m*-chloro-, and *p*-bromophenoxo complexes are shown in Fig. 3. The TG curves show two abrupt weight losses. The first abrupt weight losses, observed before 85 °C, and the corresponding endothermic DTA peaks, are due to the liberation of the crystallized thf molecules (two, two, and three moles, respectively). The second abrupt weight losses and the corresponding endothermic DTA peaks are due to the liberation 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*-bromophenoxo complexes, apparently correspond to the second color change, from blue to rose, in which the TG curves remained flat. Figure 4 depicts the results of TG-DTA analyses of 2,4-dichloro- and 2,4-dimethylphenoxo complexes. The DTA curve of the former gives two endothermic peaks corresponding to the two abrupt weight losses observed in the TG curve. The first peak, at 59 °C, is due to liberation of one mole of crystallized thf, while the second peak, at 100 °C, is due to liberation of the two coordinated thf molecules, while at the same time corresponded to the color changes 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 crystallized thf, 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. In the case of *o*-chloro- and *o*-

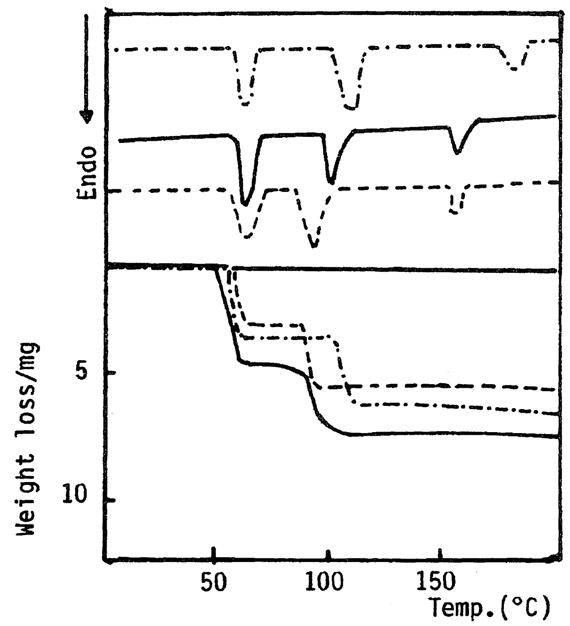

Fig. 3. TG-DTA patterns of 2,6-dichloro (- - -), *m*-chloro (–•–) and *p*-bromo (——) complexes. Heating rate: 10 °C min^{-1}; DTA sensitivity ±25 μV; gas flow: N_2, 200 mL min^{-1}; amounts of samples; 20.4, 19.6, and 22.4 mg, respectively.

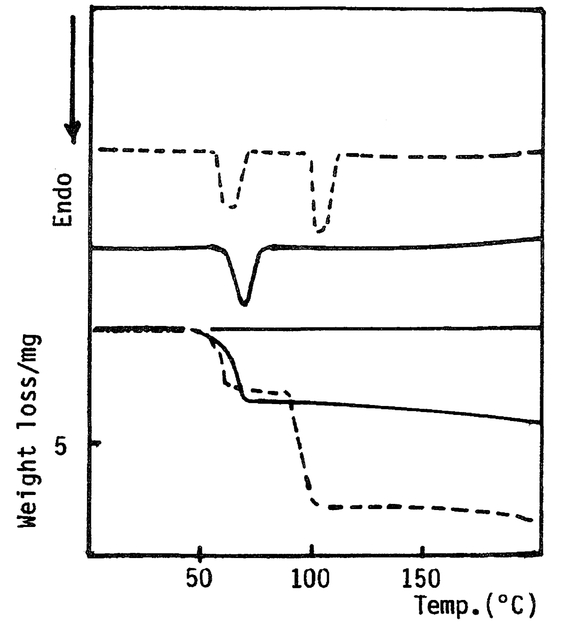

Fig. 4. TG-DTA pattern of 2,6-dichloro (- - -) and 2,4-dimethyl (—) complexes. Heating rate: 2 °C min^{-1}. DTA sensitivity; ±25 μV; gas flow: N_2 at 200 mL min^{-1}, amounts of samples: 34.5 and 28.1 mg, respectively.

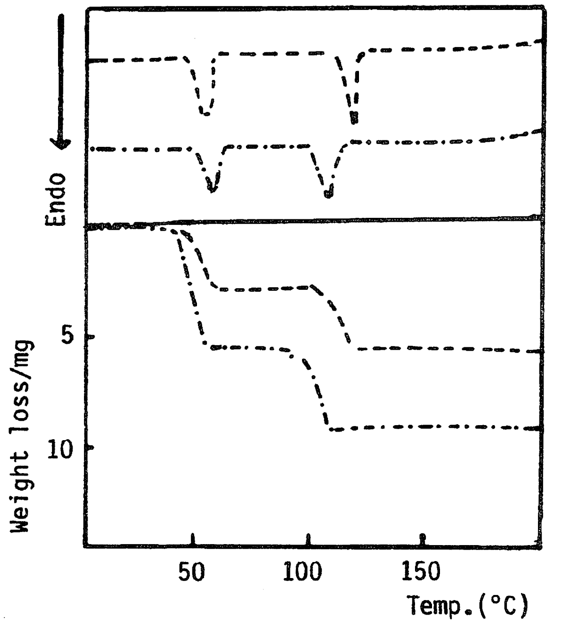

Fig. 5. TG-DTA patterns of *o*-bromo (- - -) and *o*-chloro (– • –) complexes. Heating rate: 5 °C min^{-1}. DTA sensitivity: ±25 μV; gas flow: N_2 200 mL min^{-1}; amounts of samples 21.37 and 25.37 mg, respectively.

bromophenoxo complexes (Fig. 5), the first abrupt weight losses observed in both TG curves and the corresponding endothermic peaks at 63 and 58 °C are due to the liberation of three and two moles of crystallized thf, respectively. The second abrupt weight losses observed and the corresponding DTA peaks at 113 and 125 °C, are due to the liberation of the two coordinated thf molecules, which are responsible for the color change from violet to rose. The results obtained by TG-DTA analyses of the studied complexes are summarized in Table 2. The enthalpy changes for the reaction of the type (blue→rose), are also shown in Table 2 and were estimated from the DSC measurements done separately.

Spectral and Magnetic Changes of the Complexes. Figure 1 gives a comparison of the spectra of obtained blue and rose species of the 2,6-dichlorophenoxo complex with the spectrum of the original violet complex. As shown in the Fig. 1, it is clear that, the spectrum of the blue product shows drastic spectral changes and a broad band with higher intensity characteristic of tetrahedral Co(II) appears.[16] 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 is due to the formation of an aryloxo-bridged polymer.[16,17] The spectra of the rose products of *o*-chloro- and *o*-bromophenoxo complexes are shown in Fig. 6, which are identical with those of the original violet complexes. The spectra of the obtained blue products of 2,4-dimethyl- and

Table 2. The Results of Thermal Analyses

Complex	Desolvation		$T_d \rightarrow O_h$ Transformation	
	Temp/°C	Weight loss/ %[a)]	Temp/°C	ΔH/kJ mol^{-1}
$Na_2[Co(2,6–_2C_6H_3O)_4(thf)_2]\cdot 2thf$	57—74	13.69 (13.83)	150—162	6.95
	85—98	27.43 (27.69)		
$Na_2[Co(2,4-Cl_2C_6H_3O)_4(thf)_2]\cdot thf$	53—66	6.98 (7.43)		
	95—108	21.89 (22.29)		
$Na_2[Co(2,4-Me_2C_6H_3O)_4]\cdot thf$	56—72	10.33 (10.88)		
$Na_2[Co(o–ClC_6H_4O)_4(thf)_2]\cdot 3thf$	48—65	21.85 (22.14)		
	105—116	36.29 (36.90)		
$Na_2[Co(m–ClC_6H_4O)_4(thf)_2]\cdot 2thf$	55—71	15.37 (15.95)	172—188	23.80
	100—120	31.45 (31.88)		
$Na_2[Co(o–BrC_6H_4O)_4(thf)_2]\cdot 2thf$	49—68	12.89 (13.32)		
	113—128	25.98 (26.64)		
$Na_2[Co(p–BrC_6H_4O)_4(thf)_2]\cdot 3thf$	58—70	21.23 (20.52)	149—163	7.68
	95—107	33.75 (34.20)		

a) Calculated values are in parentheses.

2,4-dichlorophenoxo complexes (for 2,4-dimethylphenoxo complex, the spectrum of the thermal product was measured for a blue species obtained at a higher temperature than those at which the other blue products were formed) are shown in Figs. 7 and 8. 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 are a drastic spectral changes and bands characteristic of the tetrahedral configuration appear.[16)]

The magnetic susceptibilities for the obtained thermal products are given in Table 1. The data shows drastic changes in the moments of the blue products from those of the original complexes, corresponding to configurational changes from octahedral to tetrahedral structures. The magnetic moments measured for the rose products indicate their octahedral configurations. The lowering (ca. 5%) in the μ values measured for the rose products compared to those of the original violet complexes is attributed to the antiferromagnetic interactions between Co(II) ions in the octahedral aryloxo bridged polymers. The magnitude of the magnetic moments (Table 1) at room temperature indicates that the complexes have high-spin configuration. The magnetic susceptibilities have been also measured at temperatures of 80—300 K (Table 3), for the original violet complex $Na_2[Co(o\text{-}ClC_6H_4O)_4(thf)_2]$, and its rose product. Both complexes have Curie or Curie–Weiss behavior,[16)] which is consistent with the lattice based on the MO_6 octahedron. The magnetic moment of the original violet complex has the marked temperature dependence that characterizes strongly linear antiferromagnetic systems. On the other hand, the observable temperature dependence (Table 3) of the magnetic properties of the corresponding rose product is that expected[18)] for a trimeric molecule involving triangular metal clusters with weak metal-metal interaction. The trimeric structure given in Fig. 9 satisfies both stoichiometric and the stereochemical requirements. Similar trimeric structures were reported[19,20)] for $[Co(bpy)_2Cl_2]$ and $[Ti(OEt)_4]_3$.

IR Spectra. All complexes show the characteristic ν(C=C) of the aromatic ring at ca. 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[21)] to ν(C–O–C) of the thf molecule, 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 frequencies (ca. 450 cm^{-1}) than its value in the case of the blue or violet complexes (ca. 490 cm^{-1}). The shift in ν(Co–O) (40 cm^{-1}), indicates the polymeric structure of the rose prod-

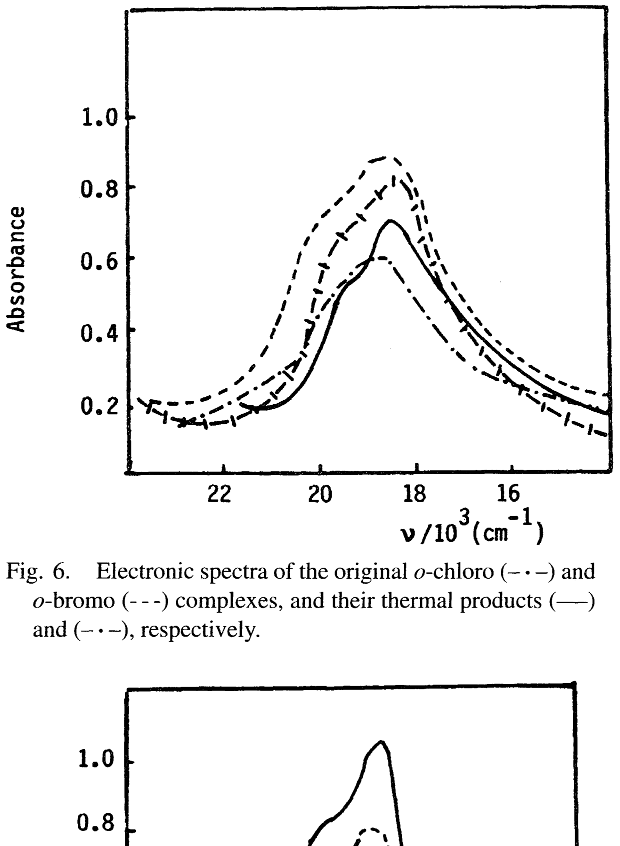

Fig. 6. Electronic spectra of the original o-chloro (– • –) and o-bromo (- - -) complexes, and their thermal products (——) and (– • –), respectively.

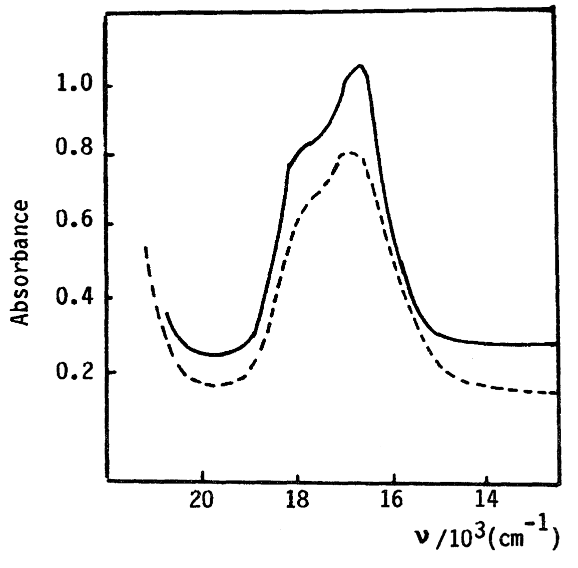

Fig. 7. Electronic spectra of the original 2,4-diemthyl complex (——) and its thermal product.

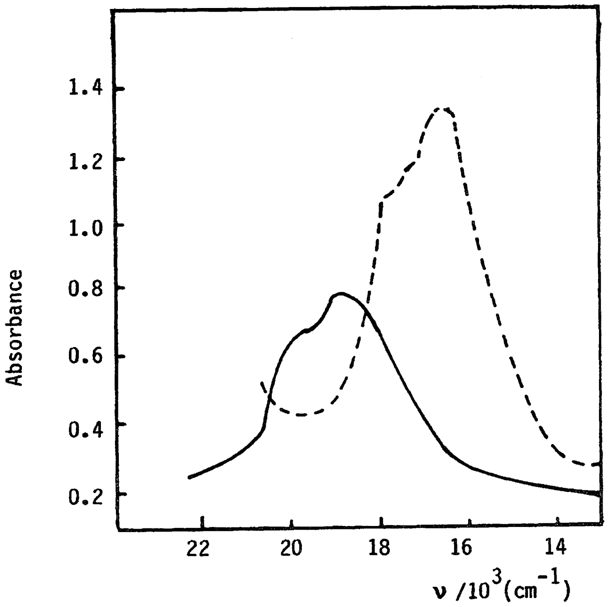

Fig. 8. Electronic spectra of the original 2,4-dichloro complex (——) and its thermal blue product.

Table 3. Variable Temperature Magnetic Susceptibilities Data for $Na_2[Co(o\text{-}ClC_6H_4O)_4(thf)_2]\cdot3thf$ and $-[-Na_2[Co(o\text{-}ClC_6H_4O)_4]-]_n-$ Complexes

Temp	$Na_2[Co(o\text{-}ClC_6H_4O)_4(thf)_2]\cdot3thf$		$-[-Na_2[Co(o\text{-}ClC_6H_4O)_4]-]_n-$	
K	$\chi_M\cdot10^{-6}$	μ_{eff}	$\chi_M\cdot10^{-6}$	μ_{eff}
	CGS	B.M.	CGS	B.M.
82	21987	3.80	34356	4.75
102	21088	4.15	28204	4.80
112	20613	4.30	26767	4.90
130	20324	4.60	24012	5.00
145	19022	4.70	21874	5.04
164	19034	5.00	19570	5.07
180	18398	5.15	18042	5.10
220	15643	5.25	14762	5.10
265	12987	5.25	12497	5.15
273	12751	5.28	12131	5.15
295	1799	5.28	11313	5.17

ucts as confirmed[22] by the values of its magnetic moments. Bochmann[23] has reported stretching frequencies of 718 and 555 cm^{-1} for M–O of the monomeric $Cr(OCHBu^t{}_2)_4$ and the dimeric $LiCr(OCHBu^t{}_2)_3\cdot thf$, respectively. Also Komiya[24] reported a stretching frequency of 1290 cm^{-1} for (C–O)Fe in $Fe(OPh)_2(bpy)_2$. 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, ν_1(10Dq), of Co(II) ions.[16] The disappearance of these broad bands in the IR spectra of the rose products confirms the configurational transformations, $T_d\rightarrow O_h$, accompanied by color changes from blue to rose. Table 4, summarizes the observed stretching frequencies of ν(Co–O), ν(C–O–C), and ν(C–O). Intensity measurements[25] of the bridging Co–O bands (in both the original violet and the rose complexes) is used to estimate the number of polymerization in the rose products. The result is ca. 1 : 3 for $(Co\text{–}O)_{violet} : (Co\text{–}O)_{rose}$ which is in harmony with the proposed structure for the rose products. On the other hand, only one stretching band of the Co–O bond is observed in the IR spectra of the original violet complexes, which reflected the symmetry of the coordinate bond skeleton in these complexes[26] being D_{4h}. Therefore, these complexes can be formulated as *trans*-$Na_2[Co(OAr)_4(thf)_2]$ as depicted in Fig. 9. The positions of sodium ions could be understood on the basis of a "coordination model" in which the complex adopts the smallest possible structural unit consistent with all atoms attaining their higher coordination number.[27]

Mass Spectra. The polymeric behaviour of the rose complexes is confirmed by the mass spectral study of the rose product of the *o*-chloro-derivative as an example of this type of complex. The mass spectrum shows that the highest mass fragment corresponded to $[NaCo_3(o\text{-}ClC_6H_4O)_6]^+$, (*m*/*z* 965;

Table 4. Characteristic Infrared Bands of the Complexes

Complexes	ν(C–O)Co	ν(Co–O)	ν(C–O–C)	$\nu[^2A_2\rightarrow{}^4T_2]$
	cm^{-1}	cm^{-1}	cm^{-1}	(10 Dq) cm^{-1}
$Na_2[Co(2,6\text{–}Cl_2C_6H_3O)_4(thf)_2]\cdot2thf$	1195, 1170	505	1080	
$Na_2[Co(2,6\text{–}Cl_2C_6H_3O)_4]$	1185, 1150	490		3544
$-[-Na_2[Co(2,6\text{–}Cl_2C_6H_3O)_4]-]_n-$	1190, 1160	430, 410		
$Na_2[Co(2,4\text{–}Cl_2C_6H_3O)_4(thf)_2]\cdot thf$	1185, 1170	505	1050	
$Na_2[Co(2,4\text{–}Cl_2C_6H_3O)_4]$	1160, 1150	420		3535
$Na_2[Co(2,4\text{–}Me_2C_6H_3O)_4]\cdot thf$	1225, 1200	550	1030	3575
$Na_2[Co(2,4\text{–}Me_2C_6H_3O)_4]$	1205, 1190	495		3550
$Na_2[Co(o\text{–}ClC_6H_4O)_4(thf)_2]\cdot3thf$	1185, 1160	490	1020	
$-[-Na_2[Co(o\text{–}ClC_6H_4O)_4-]_n-$	180,1150	444		
$Na_2[Co(m\text{–}ClC_6H_4O)_4(thf)_2]\cdot2thf$	1190, 1165	504	1070	
$Na_2[Co(m\text{–}ClC_6H_4O)_4]]$	1185, 1160	490		
$-[-Na_2[Co(m\text{–}ClC_6H_4O)_4]-]_n-$	1165, 1140	435		
$Na_2[Co(o\text{–}BrC_6H_4O)_4(thf)_2]\cdot2thf$	1180, 1150	510, 494	1065	
$-[-Na_2[Co(o\text{–}BrC_6H_4O)_4]-]-_n$	1175, 1155	441		
$Na_2[Co(p\text{–}BrC_6H_4O)_4(thf)_2]\cdot3thf$	1205	500	1025	
$Na_2[Co(p\text{–}BrC_6H_4O)_4]$	1190, 1170	485		3495
$-[-Na_2[Co(p\text{–}BrC_6H_4O)_4]-]_n-$	1175	440		

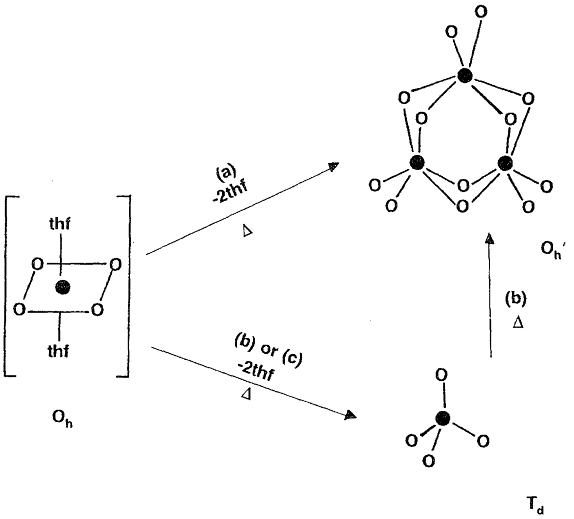

Fig. 9. Thermal reaction scheme of $Na_2[Co(OAr)_4(thf)_2]$ complexes; reaction (a) $O_h \rightarrow O_h'$ for OAr = o − chloro, or o-bomophenoxo, reaction (b) $O_h \rightarrow T_d \rightarrow O_h'$ for OAr = 2,6 − dichloro, m-chloro or p-bromophenoxo, and reaction (c) $O_h \rightarrow T_d$ for OAr = 2,4 − dichlorophenoxo, where ● = cobalt and ○ = oxygen.

7.8%), which losses Na(o-ClC_6H_4O) to give the fragment $[Co_3(o\text{-}ClC_6H_4O)_5]^+$, ($m/z$ 812; 9.5%). Also, the observed ion $[Co_3(o\text{-}ClC_6H_4O)_4(OC_4H_3)]^+$ arise further loss of C_2HCl from the m/z 752 fragment. The mass fragmentation pattern indicates the presence of some dimeric species with lower abundance that arise from the fragmentation of the trimeric species. Also the spectrum shows that the largest number of mass ion peaks is present in the trimeric region, which is ascribed to the trimeric form of this complex. On the other hand, the mass spectrum of the corresponding original violet complex, $Na_2[(Co(o\text{-}ClC_6H_4O)_4(thf)_2]\cdot 3thf$, shows a $[Co(o\text{-}ClC_6H_4O)_2]^+$ fragment with higher abundance. In both mass spectra, no parent molecular ion peaks are observed.

Effects of the Substituent Groups of the Phenoxide Ring upon the Transformation. The thermal reactions of those complexes that are accompanied by distinct color or structural changes can be classified into the following three types:

$$\text{(a)}\quad Na_2[Co(OAr)_4(thf)_2]\ (O_h) \xrightarrow{-2thf/\Delta} -[-Na_2[Co(OAr)_4-]_n-\ (O_h')$$

$$\text{(b)}\quad Na_2[Co(OAr)_4(thf)_2]\ (O_h) \xrightarrow{-2thf/\Delta} Na_2[Co(OAr)_4]\ (T_d) \xrightarrow{\Delta} -[-Na_2[Co(OAr)_4-]_n-\ (O_h')$$

$$\text{(c)}\quad Na_2[Co(OAr)_4(thf)_2]\ (O_h) \xrightarrow{-2thf/\Delta} Na_2[Co(OAr)_4]\ (T_d)$$

here, O_h (or O_h') and T_d represent an octahedral species and/or a desolvated tetrahedral one.

In o-substituted phenoxo complexes, only reactions of type (a) are observed on heating; no blue tetrahedral species are formed. The O_h' complexes obtained do not show any structural changes until they decomposed on strong heating. This situation is probably due to the fact that, in these complexes, substituent groups exert highly selective influence on the stabilities of the complexes. On the other hand, 2,6-dichloro-, 2,4-dichloro-, m-chloro-, and p-bromophenoxo complexes undergo thermal reactions either of type (b) or (c), which include the formation of the tetrahedral species. In these complexes the substituent groups tend to lower the ligand field strength, thus tetrahedral species do occur. However, the mode of thermal reactions seems to depend on more complicated structural factors. Figure 9 shows the structural formulae of these changes. In case of 2,4-dimethylphenoxo complex, the steric hindrance of the two methyl groups seems to play the main role in retaining its tetrahedral configuration upon heating.

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