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Spectral and thermal studies of solid-phase thermochromism of Co(II) double metal complexes

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Abstract

Tetrahedral solid state structures of the blue potassium tris(aryloxo)cobaltate(II)-tetrahydrofurane complexes of the formula KCo(OAr)₃·2thf (OAr = o-chloro-, o-bromo-, m-chloro-, p-bromo, 2,6-dichloro-, 2,4-dichloro- or 2,4-dimethylphenoxide) undergo solid-phase thermal tetrahedral to octahedral transformation accompanied by change in their colours from blue to rose (one-step thermochromism). Magnetic moments, electronic and infrared spectral studies supported these results. Thermal treatment of theses complexes leads to the loss of the crystallized thf molecule yielding also blue tetrahedral complexes. However, further heating leads to the loss of the coordinated th molecule and the formation of rose octahedral trimeric products. TG-DTA results showed that the, two solvated thf molecules were eliminated in two steps. Mass spectral studies and IR intensity measurements confirmed the trimeric behaviour of the rose octahedral geometry of thermal products. Conductance measurements of solutions of these complexes in thf indicated that they behave as non-electrolytes. © 2006 Elsevier B.V. All rights reserved.

Keywords: Thermochromism; T_d to O_h transformation

1. Introduction

The alkyloxo (-OR) and the aryloxo (-OAr) groups have been of considerable interest to the coordination chemist due to their ability to form strong covalent bonds with almost all metals. Also, their tendency to act as bridges between similar as well as different metal atoms [1]. A considerable amount of work has been done on metal alkyloxides due to their use in many organic synthesis and their industrial applications [1-3]. Also, much work has been done on double alkyloxides involving more than one metal atom within the molecular species [1–3]. Thus, alkali metal alkyloxonickolate(II) have been used as a new catalyst of higher activity in nickel-catalyst system [4]. In addition, alkyloxocobaltate(II) complexes of the formula MM'(OR)₄(MBr)_{*m*}·*n*thf, M = Li, Na or K, M' = Ni or Co, R = ethyl, isopropyl, isobutyl, sec-butyl, pent-3-yl, menth-3-yl, allyl, or benzyl (m = zero; M = Na or K, m = 1-2; M = Li and n = 1-6, have been prepared and characterized [5-8]. On the other hand, very little work has been reported on the corresponding aryloxo derivatives especially for cobalt(II). We report

1386-1425/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2006.11.015 in this work the synthesis and thermal reactions of potassium tris(aryloxo)cobaltate tetrahydrofurane complexes of the formula $KCo(OAr)_3 \cdot 2thf$.

2. Results and discussion

2.1. Synthetic, electronic and magnetic studies of the original complexes 1–7

Under anaerobic conditions anhydrous CoBr_2 or $\text{CoBr}_2 \cdot 2\text{thf}$ reacts with a solution of the potassium salt of *o*-chloro-, *o*-bromo-, *m*-chloro-, *p*-bromo-, 2,6- dichloro-, 2,4-dichloro-, or 2,4-dimethylphenol (abbreviated as KOAr) in thf; molar ratio KOAr/Co(II) ≥ 4 , where air-sensitive potassium tris(aryloxo)cobaltate(II) complexes·2thf are obtained as blue or blue violet solids. In contrast to K₂Co(Oph)₄·thf complex previously reported [7], the obtained complexes, **1–7**, Table 1, contain only three aryloxide moieties per each molecular unit in spite of the presence of excess KOAr in the reaction mixtures. This could be attributed to the bulk of the OAr moieties beside the bridged potassium ion, which may hindered the coordination of the fourth OAr moiety. The structure of the complexes is indicated as follows.

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The amount of the reactants used, the conditions followed to isolate the solid complexes 1									
No.	Complex	Amount of the reactants used (g) mmol		Colour of the solution	Conditions of the isolation	Yield (g) %	Analysis (cald.) found		
		CoBr ₂ [*] or CoBr ₂ 2thf	KOAr				K	Со	OAr
1	KCo(o-ClC ₆ H ₄ O) ₃ ·2thf	(7.00) 19.3	(12.9) 77.0	Blue violet	a	(7.3) 61.0	(6.3) 6020	(9.4) 9.2	(61.2) 61.7
2	KCo(o-BrC6H4O)3.2thf	$(5.90) 27.0^{*}$	(22.8) 108	Blue violet	а	(12.5) 57.0	(5.2) 5.0	(7.8) 7.5	(68.1) 67.4
3	KCo(m-ClC ₆ H ₄ O) ₃ ·2thf	(7.90) 21.8	(14.4) 86.0	Blue violet	b	(7.5) 55.0	(6.3) 6.40	(9.4) 9.7	(61.2) 61.5
4	KCo(p-BrC6H4O)3.2thf	(6.50) 29.7*	(25.0) 119	Deep blue	а	(14.7) 65.9	(5.2) 5.30	(7.8) 7.5	(68.1) 76.7
5	KCo(2,4-Cl ₂ C ₆ H ₃ O) ₃ ·2thf	(8.80) 24.2	(19.5) 97.0	Deep blue	b	(9.5) 54.0	(5.4) 5.50	(8.1) 8.3	(66.8) 67.0
6	KCo(2,6-Cl ₂ C ₆ H ₃ O) ₃ ·2thf	(8.20) 22.6	(18.2) 91.0	Deep blue	с	(8.2) 49.0	(5.4) 5.20	(8.1) 8.4	(66.8) 67.1
7	KCo(2,6-(Me) ₂ C ₆ H ₃ O) ₃ ·2thf	(4.85) 22.2*	(14.0) 90.0	Blue	с	(8.3) 62.9	(6.5) 6.30	(9.7) 9.9	(60.0) 60.5
6 7	$ \begin{array}{l} KCo(2,6\text{-}Cl_2C_6H_3O)_3\cdot 2thf \\ KCo(2,6\text{-}(Me)_2C_6H_3O)_3\cdot 2thf \end{array} \\ \end{array} $	(8.20) 22.6 (4.85) 22.2 [*]	(18.2) 91.0 (14.0) 90.0	Deep blue Blue	c c	(8.2) 49.0 (8.3) 62.9	(5.4) 5.20 (6.5) 6.30		(8.1) 8.4 (9.7) 9.9

Table 1 The amount of the reactants used, the colour, the conditions followed to isolate the solid complexes 1–7

(a) The concentrated solution was left for 7 days at -78 °C, after which the precipitated crystals were isolated, (b) 5 ml *n*-hexane was added to the concentrated solution previously cooled at -78 °C for 10 days, (c) the concentrated solution was left for 15 days at -78 °C, after which, 20 ml cooled *n*-hexane was, (d) added and then the mixture was left for further 4 days at -78 °C after which the precipitated solid complex was isolated.



The prepared complexes were highly air-sensitive as the previously reported alkyloxo complexes of Co(II) and Ni(II) of the formula KCo(OR)₃·thf and KNi(OR)₃·thf [5–7]. The complexes decomposed immediately by addition of water. They react with compounds containing acidic-H of pK^{H} -values smaller than that of the appropriate phenol. Thus, through the reaction of 2,4dichlorophenol with 7, we have obtained 5. Electronic spectral data and magnetic moments measurements are given in Table 2. As shown in Table 2, all the prepared solid complexes 1–7 have magnetic moments in the range 4.48-4.62 B.M. and absorb strongly in the range $16,400-17,300 \text{ cm}^{-1}$. A main absorption band appeared at $\sim 16,500 \,\mathrm{cm}^{-1}$ which have high values of extinction coefficients (Table 2 and Fig. 1). These properties are characteristic of spin-free tetrahedral cobalt(II) complexes [9]. The tetrahedral structure would be accomplished through the attachment of three aryloxide groups and one thf molecule to the cobalt(II) cation.

2.2. Thermochromism of the original complexes 1–7

Fig. 2 shows the results of visual observations on the solidphase thermochromism of complexes 1-7. All complexes show



Fig. 1. Electronic spectra of the di-solvated complex, 3(--) and its thermal products 3a(---) and 3b(----).

one-step thermochromism from blue to the rose, non-solvated, products **lb–7b**. The colour changes are reversible. The reverse changes proceed on cooling the rose products to room temperature and introducing dry thf-vapour into the system. The rose product absorb thf molecules gradually and revert to the original di-solvated complexes **1–7** in several hours or days. The time taken in the reversible reactions as well as the temperature ranges at which the rose products are formed seems to be affected by the group(s) present in the phenoxide ring [10]. All the rose non-solvated thermal products **lb–7b** are stable and could be isolated and identified. Analytical data of the com-



Fig. 2. Results of visual observations of the thermochromic changes of the complexes, b: blue or blue violet, R: rose. The rose colour appears at the spots shown; the right-hand ends of the lines corresponded to the decomposition points.

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Electronic spectral data, magnetic moments and IR-vibration^a frequencies, of the original complexes, 1–7, and the corresponding thermal products, 1a–7a and 1b–7b

No.	Complex	Absorption maxima $v 10^{-3} (\text{cm}^{-1})$	$\mu_{\rm eff.}$ (B.M.)	ν(Co–O) (cm ⁻¹)	ν(C–O–C) (cm ⁻¹)	${}^{4}A_{2}(F) \rightarrow {}^{4}T_{2}(F)$ 10Dq (cm ⁻¹)
1	$KCo(\textit{o-ClC}_6H_4O)_3{\cdot}2thf$	16.525 16.550	4.48	665	1055	3580
1a	$KCo(\textit{o-ClC}_6H_4O)_3{\cdot}thf$	16.665 16.750	4.19	690	1050	3490
1b	KCo(o-ClC ₆ H ₄ O) ₃	19.960 20.700	5.15	450	-	_
2	KCo(o-BrC ₆ H ₄ O) ₃ ·2thf	16.500 16.650	4.60	575	1070	3585
2a	$KCo(\textit{o-BrC}_6H_4O)_3thf$	16.660 16.750	4.55	625	1055	3590
2b	KCo(o-BrC ₆ H ₄ O) ₃	19.900 20.500	5.25	440	-	-
3	KCo(m-ClC ₆ H ₄ O) ₃ ·2thf	16.650 17.450	4.61	620	1060	3590
3a	KCo(m-ClC ₆ H ₄ O) ₃ ·thf	16.600 16.750	4.56	630	1045	3580
3b	KCo(m-ClC ₆ H ₄ O) ₃	19.800 20.900	5.22	450	-	_
4	KCo(p-BrC ₆ H ₄ O) ₃ ·2thf	16.700 17.450	4.58	675	1070	3585
4a	KCo(<i>p</i> -BrC ₆ H ₄ O) ₃ ⋅thf	16.680 17.750	4.49	620	1055	3575
4b	$\text{KCo}(p-\text{BrC}_6\text{H}_4\text{O})_3$	19.870 20.600	5.23	450	-	-
5	$KCo(2,4\text{-}Cl_2C_6H_3O)_3\text{-}2thf$	16.600 17.350	4.61	620	1055	3580
5a	$KCo(2,4\text{-}Cl_2C_6H_3O)_3\cdot thf$	16.770 17.555	4.55	620	1050	3575
5b	KCo(2,4-Cl ₂ C ₆ H ₃ O) ₃	19.980 20.400	5.15	470	-	-
6	$KCo(2,6\text{-}Cl_2C_6H_3O)_3\cdot 2thf$	16.800 17.500	4.62	695	1055	3590
6a	$KCo(2,6\text{-}Cl_2C_6H_3O)_3\cdot thf$	16.770 17.300	4.50	615	1050	3585
6b	KCo(2,6-Cl ₂ C ₆ H ₃ O) ₃	19.980 20.650	5.17	420	_	-
7	$KCo(2,6-(Me)_2C_6H_3O)_3\cdot 2thf$	16.500 16.800	4.58	630	1070	3575
7a	$KCo(2,6-(Me)_2C_6H_3O)_3\cdot thf$	16.900 19.900	4.60	620	1055	3585
7b	KCo(2,6-(Me) ₂ C ₆ H ₃ O) ₃	20.550	5.23	455	_	-

^a ν (Co-Cl) 780, ν (Co-Br) 755 cm⁻¹.

plexes **lb**–**7b** is summarized in Table 3 correspond to the formula KCo(OAr)₃.

2.3. Thermal analyses

The results of TG-DTA for the complexes 1–7 are shown in Figs. 3 and 4 and Table 4. All the complexes liberate the thf molecules in two steps. The first abrupt weight loss observed in the TG-curves before 95 °C and the corresponding endothermic DTA peaks, are due to the liberation of the crystallized (non-coordinated) thf molecule. At this stage, the blue colours of the complexes were unchanged as deduced from the visual thermal observations (Fig. 2). The second abrupt weight loss at 125–181 °C and the corresponding endothermic DTA peaks are due to the splitting of the second coordinated thf molecule, at this stage the complexes change their colour to rose. After that, the plateau, in the TG curves remain flat until the decomposition of the complexes. The differences in the temperature ranges, at which these rose products were formed attributed to the differences in the electronic properties and the steric requirements of the ligand used. The thermal treatment led us to isolate the intermediate monosolvated complexes, $KCo(OAr)_3$ ·thf, **1a–7a** (Table 3) formed during the thermal reactions of the original complexes **1–7**. The enthalpy changes, Table 4, for the reactions of the type blue, mono-solvated, to the rose non-solvated products were

Table 5	
Analytical data of the blue mono-solvate	ed 1a-7a and the rose non-solvated
1b–7b complexes	

No.	Complex	Analysis (cald.) found				
		K	Со	OAr		
1a	KCo(o-ClC ₆ H ₄ O) ₃ ·thf	(7.1) 7.0	(10.7) 11.0	(69.2) 70.1		
1b	KCo(o-ClC ₆ H ₄ O)	(8.1) 7.9	(12.3) 12.5	(79.6) 80.1		
2a	$KCo(o-BrC_6H_4O)_3 \cdot thf KCo(o-BrC_6H_4O)_3$	(5.7) 8.9	(8.6) 8.9	(75.2) 74.6		
2b		(6.4) 6.2	(9.6) 9.3	(84.0) 83.6		
3a	$KCo(m-ClC_6H_4O)_3 \cdot thf$	(7.1) 7.3	(10.7) 11.0	(69.6) 6.8.9		
3b	$KCo(m-ClC_6H_4O)_3$	(8.1) 7.8	(12.3) 12.8	(79.6) 79.3		
4a	KCo(<i>p</i> -BrC ₆ H ₄ O) ₃ ·thf	(5.7) 6.2	(8.6) 8.9	(75.2) 75.7		
4b	KCo(<i>p</i> -BrC ₆ H ₄ O) ₃	(6.4) 6.8	(9.6) 9.9	(84.0) 83.8		
5a	$\begin{array}{l} KCo(2,4\text{-}Cl_{2}C_{6}H_{3}O)_{3}\text{\cdot}thf \\ KCo(2,4\text{-}Cl_{2}C_{6}H_{3}O)_{3} \end{array}$	(6.0) 6.4	(9.0) 8.7	(74.1) 74.6		
5b		(7.0) 6.3	(10.1) 10.5	(83.2) 82.8		
6a	$\begin{array}{l} KCo(2,6\text{-}Cl_2C_6H_3O)_3 \cdot thf \\ KCo(2,6\text{-}Cl_2C_6H_3O)_3 \end{array}$	(6.0) 5.6	(9.0) 8.3	(74.1) 74.6		
6b		(7.0) 6.6	(10.1) 9.7	(83.2) 82.8		
7a	$ \begin{array}{l} KCo(2,6\text{-}(Me)_2C_6H_3O)_3 \text{\cdot}thf \\ KCo(2,6\text{-}(Me)_2C_6H_3O)_3 \end{array} $	(7.3) 7.0	(11.0) 10.7	(68.1) 68.6		
7b		(8.5) 8.2	(12.8) 13.1	(78.8) 80.0		

estimated from the DSC measurements carried out separately. (Fig. 4).

2.4. Spectral and magnetic changes on heating the solid original complexes **1**–7

Spectral and magnetic moment data for the original disolvated complexes 1–7 and the isolated thermal products **la–7a** and **lb–7b** are collected in Table 1. Fig. 1 gives a comparison of the visible spectra of the thermal products **3a** and **3b** with the spectrum of the original blue di-solvated complex, **3**, as an example of the spectral changes on heating these types of complexes. As shown in figure, it is clear that the spectrum of the blue mono-

Table 4 Results of TG-DAT and DSC thermal analysis of the solid complexes 1–7



Fig. 3. TG-DTA of 1(—), 2(...), 3(----), 4(---) complexes. Heating rate $20 \,^{\circ}$ C min⁻¹; DTA sensitivity $\pm \mu$ V; amount of sample of 1–4 complexes are: 26.5, 22.9, 19.9 and 17.6 mg, respectively.

solvated complex, 3a, remains nearly unchanged after liberation of one molecule thf from the original complex 3, indicating that the tetrahedral configuration is retained [9]. On the other hand, the spectrum of the non-solvated rose product, 3b, show spectral changes where broad bands of lower intensities, characteristic of octahedral Co(II) appear [9,10]. The following equation could be such equilibrium (Fig. 5).

KCo(OAr) ₃ .2THF	KC₀(OAr) ₃ .THF - TH	[⊮] → -[-KCo(OAr) ₃ -]- _n
T_{d} (1-7)	$T_d (1_a - 7_a)$	$O_h (1_b - 7_b)$
	Type (a) complexes	Type (b) complexes

The visible spectra of complexes of "**a**" type generally show a main absorption band at $\sim 16,500 \text{ cm}^{-1}$ and a shoulder at $\sim 172,500 \text{ cm}^{-1}$. Their magnetic moments are in the range 4.19–4.56 B.M. which are somewhat lower than the values of the

No.	Complex	Desolvation		Decomposition	$\Delta H (\mathrm{kJmol}^{-1})T_\mathrm{d}$ to	
		Temperature (°C)	Weight loos (calcd.) found (%)	Temperature (°C)	<i>O</i> _h transformation	
1	KCo(o-ClC ₆ H ₄ O) ₃ .2thf	66–91 135–157	(11.5) 11.1 (23.1) 22.7	245	- 13.7	
2	KCo(o-BrC ₆ H ₄ O) ₃ .2thf	66–95 128–155	(9.5) 9.2 (19.0) 18.4	245	_ 11.50	
3	KCo(m-ClC ₆ H ₄ O) ₃ .2thf	60–85 130–163	(11.5) 11.0 (23.1) 22.6	250		
4	KCo(p-BrC ₆ H ₄ O) ₃ .2thf	68–90 144–168	(9.5) 9.2 (19.0) 18.6	250	_ 10.70	
5	$KCo(2,4\text{-}Cl_2C_6H_3O)_3.2thf$	70–86 136–181	(9.9) 10.4 (19.8) 19.1	235	- 12.76	
6	$KCo(2,6\text{-}Cl_2C_6H_3O)_3.2thf$	70–95 140–171	(9.9) 9.4 (19.8) 19.3	237		
7	$KCo(2,6-(Me)_2C_6H_3O)_3.2thf$	71–92 145–178	(11.9) 11.4 (23.8) 23.3	240	-	



Fig. 4. TG-DTA of 5(—), 2(...), 6(---), 7(----) complexes. Heating rate $20 \,^{\circ}\text{C} \text{min}^{-1}$; DTA sensitivity $\pm \mu V$; amount of sample of 5–7 complexes are: 18.50, 21.2, and 23.6 mg, respectively.

original complexes. Thus, the decrease in the number of crystallized thf molecules leads to the decrease of their magnetic moments. This may be attributed to the increase of antiferromagnetic interactions between adjacent Co(II) cations. On the other hand, the visible spectra of complexes of "**b**" type show a main absorption bands at $-19,100 \text{ cm}^{-1}$ and a shoulder at 20,700 cm⁻¹. Their magnetic moments are in the range 5.15-5.23 B.M. The change in the colour of the complexes (blue to rose) upon heating coupled with the change in spectral and magnetic moments data are attributed to the formation of octahedral trimeric products comprising bridging OAr group [1–3,11].

2.5. I.R. Spectra

All complexes show the characteristic frequency of $v(C=C)_{ring}$ (>1600 cm⁻¹). The original complexes also show a band at >500 cm⁻¹ attributed to v(Co-O) [12,13]. The spectra of the thermal products **la**-7**a** show the presence of a band



Fig. 5. Thermal reaction scheme of the complexes: reaction (a) T_d to T_d , reaction (b) T_d to O_h .

at >1050 cm⁻¹ which is assigned to $v_{as}(C-O-C)$ of the thf molecules confirming its presence in these complexes. On the other hand, the spectra of the rose products lb-7b are devoid of this absorption band, besides the v(Co-O) is observed at lower frequencies (>450 cm⁻¹). This is taken as an indication of the polymeric structure of these rose complexes [10,13]. Buchmann [3] has reported stretching frequencies of 718 and $555 \,\mathrm{cm}^{-1}$ for M–O of the monomeric $\mathrm{Cr(OCHBu}_2^t)_4$ and the dimeric LiCr(OCHBu₂^t)₄ · thf, respectively. Also, Komiya [14] reported stretching frequencies of 1290 cm^{-1} for (C–O)Fe in $Fe(OPh)_2(bpy)_2$. In addition, the spectra of the original complexes show a very broad band at $3580 \,\mathrm{cm}^{-1}$ which is assigned to spin allowed transition [${}^{4}A_{2} - {}^{4}T_{2}(F)$], $\nu_{1}(10 \text{ Dq})$ of cobalt(II) ion in tetrahedral configuration [9]. The disappearance of these broad bands in the IR spectra of the thermal rose products, 1b-7b confirms the T_d to O_h transformations accompanied by colour changes from blue to rose complexes. Furthermore, intensity measurements [15] of the bridging Co-O bands (in both the original and the rose complexes) is used to estimate the number of polymerization in the rose complexes. The result is >1:3 for (Co–O)_{original}: (Co–O)_{rose} thermal products which is in harmony with the trimeric structure of the rose thermal products. Moreover, only one stretching band of the Co-O bond is observed in the IR spectra of the original rose complexes which reflected the symmetry of the coordinate bond skeleton in these complexes [16] being D_{4h} .

2.6. Mass spectra

The polymeric behaviour of the rose complexes is confirmed by the mass spectral study of the rose product of the o-chloroderivative as an example of this type of complexes. The mass spectrum shows that the highest mass fragments corresponded to $[KCo_3(o-ClC_6H_4O)_6]^+$, (*m/e* 981; 8%), which losses K(o- ClC_6H_4O) to give the fragment $[Co_3(o-ClC_6H_4O)_5]^+$, (m/e)645.5; 11%). The mass fragmentation pattertern indicates the presence of some dimeric species with lower abundance that arises from the fragmentation of trimeric species. Also, the spectrum shows that the largest number of mass ion peaks is present in the trimeric region in the spectrum, which is ascribed to form of this complex. On the other hand, the mass spectrum of the corresponding original blue complex, K[(Co(o-ClC₆H₄O)₃]·2thf, shows a $[Co(o-ClC_6H_4O)_2]^+$ fragment with higher abundance. In both mass spectra, no parent molecular ion peaks are observed.

2.7. Electrical conductance

Electrical conductance of the complexes 1–7 which were measured in thf solutions, are ranged between $1.2-1.4 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating that all complexes behave as non-electrolytes in their thf solutions. These results suggest the presence of tight ion pairs in thf. Mehrotra [1,17] attributed the non-electrolytic nature of Na₂Zr₂(OPrⁱ)₉ (in isopropanol) and of alkyloxo complexes CoCl₂·2Bu^sOH, CoCl₂·2BuⁱOH and $CoCl_2 \cdot 2Bu^tOH$ (in their parent alcohols) to the relatively low dielectric constants of the solvents.

3. Experimental

All glass apparatus with standard joints were used throughout the experiments. Stringent precautions were taken to avoid moisture and atmospheric oxygen. All preparation and subsequent handling of materials were carried out under dry argon. Also, all operations for isolation and characterization of the complexes were carried out under absolute water-free conditions (anaerobic conditions) in an argon atmosphere using Schlenktechniques [18]. Chemicals used were of AR grade. Solvents were dried over sodium metal and benzophenone and distilled under argon immediately prior to use. Anhydrous cobalt bromide was prepared by a literature method [19]. For weighing, anaerobic sample tube-technique was used.

3.1. Preparation of potassium aryloxide ligauds

All potassium aryloxide ligands were prepared by the following general procedure: A solution of 0.1 mole of the appropriate phenol in 50 ml dry thf was added drop wise, over a period of 2 h to 5.58 g (0.15 mol) clean potassium metal (in small pieces) in 60 ml thf. After complete addition of the phenol and complete removal of the evolved hydrogen gas, the mixture was maintained under reflux for 2 h. The reaction mixture was then continuously stirred at room temperature for an additional hour and then allowed to cool and left overnight. The residual potassium metal was carefully filtered in a G₄ filtration unit. The filtrate was then stored under argon. The amount of the resultant potassium aryloxide salt in the filtrate was determined analytically by diluting 1 ml of the filtrate in 10 ml distilled water and the resulted KOH was titrated against 0.1 M HC1. The concentrations of the thf solutions of the KOAr ranged between $0.75-0.9 \text{ mol dm}^{-3}$.

3.2. Preparation of the original solid complexes 1–7

Potassium tris(aryloxo)cobaltate(II).2thf were prepared by the following procedure: CoBr2 or CoBr2.2thf was reacted with such volume of a solution of KOAr of known concentration in thf in a molar ratio of KOAr/Co(II) \geq 4. The reaction mixture was stirred at room temperature for 1/2-2 h and then allowed to stand for 24 h. The white, KBr, precipitate was separated under argon atmosphere in a G₄-filtrate unit. The clear filtrate was then, concentrated in vacuo at room temperature or at a temperature of maximum 40 °C. The solution was cooled for 5-15 days at -78 °C. The obtained blue solid complexes were filtered under argon atmosphere in a G₃-filtrate unit, washed 2 times with 5 ml dry thf, dried under vacuum and finally stored under argon. In Table 1, the amounts of the reactants used, colour of the resulted solutions, colour of the isolated solid complexes, conditions of their isolation and their analytical data, are given. The obtained complexes are bromide-free products. They are soluble in toluene, dioxane, CHCl₃ and DMF.

3.3. Visual observation of thermochromic changes of the complexes 1-7

In order to study the thermal reactions of the original complexes 1–7 and the mode of their thermochromic change of each complex, which usually occurs within a temperature range of several degrees, a sample of a given complex is heated slowly to determine, firstly, the temperature at which a distinct colour change will be observed. A new sample is then, heated to the temperature at which this colour change took place, in order to obtain the non-solvated complex.

3.4. Isolation of the blue mono-solvated complexes 1a-7a

The mono-solvated complexes **la**–**7a** were obtained by heating a small amount of the finely powdered sample of the corresponding original di-solvated complexes **1–7** putted in a two-neck Schlenk tube provided with a thermometer and inand outlet device for argon gas in a silicon oil bath. The heating rate did not exceed 5 °C min⁻¹. The heating was continued until the corresponding elevated temperature, deduced from the DTA curves, at which the mono-solvated complexes are expected to form. At this temperature the sample was left to stand for further 1/2 h to ensure the removal of all liberated thf and to avoid the occurrence of the backward reaction towards the original disolvated complexes. The product was then allowed to cool under argon atmosphere to room temperature and then identified and finally stored under argon.

3.5. Isolation of the non-solvated complexes 1b-7b

A new sample was treated as above, in all cases, the heating was continued to the temperature at which the rose products were formed as deduced from the visual observations and DTA curves.

3.6. Formation of the original complexes **1–7** from the non-solvated complexes **1b–7b**

Under the presence of thf-vapour (anaerobic conditions) and in several hours or days, the rose non-solvated complexes **lb**–**7b** absorbed 2 mols of thf and reverted to the original blue disolvated complexes. The following is the analytical data of a sample (**3 and 3b**) as an example of these reversible reactions.

Complx (colour)	Elemental analysis %(calcd.) found					
	Co(II)	OAr ⁻	K			
3 (blue)	(9.4) 9.6	(61.2) 61.7	(6.3) 6.7			
3b (rose)	(12.3) 12.6	(79.6) 80.0	(6.3) 6.7			
3 (blue)	(9.4) 9.8	(61.2) 61.9	(6.3) 6.7			

3.7. Analysis and measurements

Cobalt was determined using a complexometric titration method [20]. Aryloxide groups were determined by acidbase titration [17]. Potassium was analyzed using a PEP-7 flame photometer. Electronic spectra were recorded as Nujol mulls using Carry 14-spectrophotometer. Infrared spectra were recorded as Nujol mulls or Csl pellets using a Perkin-Elmer 598 spectrometer. Mass spectra were recorded at 70 eV and 300 °C on an MS 5988 Hewlett-Packard mass spectrometer. Magnetic measurements were carried out using a Gouy balance, Johnson Matthey, Alfa products, UK, model MKI. The calibrant were Mohr's salt and HgCo(NCS)₄. The measured molar susceptibility (χ_{mol}) was corrected for diamagnetism and the μ_{exp}/μ_B was calculated from the equation $\mu = 2.84$ [mol T]^{1/2}. TG-DTA and DSC measurements were carried out using a Perkin-Elmer high temperature differential thermal analyzer, Delta series TGA7, coupled with 3700 data station. The conditions of the runs are given in the caption of Figs. 2 and 3.

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