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Tetrahedral Potassium-Aroxo-Cobaltate(II) Complexes

AISHA I. IBRAHIM
Chemistry Department, Faculty of Education,
Ain Shams University, Roxy, Cairo, Egypt.

Potassium-aroxo-cobaltate(II) complexes of the formula $KCo(O-\langle\bigcirc\rangle_x)_3 \cdot nTHF$. (where, X = *o*–$O_2N$, *o*-Cl, *o*-Br, *m*-Cl, *p*-Br, 2, 4–, 2, 6-dichloro and 2, 4 dimethyl; n = 1 or 2) have been prepared. The various physico-chemical studies indicate that the tetrahedral streo-chemistry of these complexes. In comparison with the disodium-tetra-aroxo-cobaltate(II) complexes, the steric hindrance caused by the large size of the potassium atom, suggested to be affected the 10 Dq values, the stability of the potassium-tri-aroxo-complexes, as well as their covalency nature.

INTRODUCTION

During the course of physico-chemical studies of alkali metal-aroxo-cobaltate(II) complexes, disodium-tetra-aroxo-cobaltate(II) complexes have been previously prepared and characterized[1]. As a continuation of our studies, it is desirable to investigate the analogus complexes in which the sodium atom is replaced by alkali metal atom of larger atomic size such as potassium. We, therefore, decided to prepare the potassium-aroxo-cobaltate(II) complexes and to investigate their structures.

RESULTS AND DISCUSSION

Potassium-aroxo-cobaltate(II) complexes have been prepared using the preparative method, previously disscused[1], of the reaction of $CoBr_2$ with alkali metal phenoxide derivatives. It is observed that, as the THF solution of one mole of $CoBr_2$ was added to four moles of the potassium phenoxide derivatives in THF, the solution became dark blue. Due to the high solubilities of the prepared potassium-aroxo-cobaltate(II) complexes compared with those of sodium complexes, therefore special treatment will be done to crystallized these complexes from their THF solutions. Generally the reaction mixture concentrated and three times filtrated by interval one day left between each filtration. The free KBr-filtrate cooled at 78°C for 8–20 days, at which, the solid complexes, readily crystallized. In some cases scratching and addition of dried *n*-hexane will be applied to precipetate the solid complexes.

While elemental and analytical analysis of the sodium-aroxo-complexes corresponded the formula $Na_2Co(O-\langle\bigcirc\rangle_x)_4 \cdot 2\text{–}5THF$[1], they revealed the structure formula $KCo(O-\langle\bigcirc\rangle_x)_3 \cdot 2THF$ for the potassium complexes. The presence of less coordinated ArO^- number's could be attributed to the steric hinderance of the large size of the potassium atom.

Elemental and analytical analysis together with the colour of the complexes are summarised in Table 1. Generally complexes of this type are senstive to moisture and air[3-8], therefore precautions were taken to avoid moisture and the atmospheric oxygen.

TABLE 1
ELEMENTAL AND ANALYTICAL DATA OF POTASSIUM-TRI-AROXO-COBALTATE(II) · nTHF AND THE RESULTING PRODUCTS FROM HEATING*

Complex/Colour	Found (Calcd). %				
	Co	K	OAr	C	Cl
$KCo(o\text{–}NO_2C_6H_4O)_3 \cdot nTHF$[a]	8.71	5.48	64.90	—	—
(dark olive green)	(8.71)	(5.48)	(64.90)	—	—
$KCo(2,6\text{–}Cl_2C_6H_3O)_3 \cdot 2THF$[b]	7.93	5.26	67.99	43.65	9.67
(blue)	(8.10)	(5.37)	(66.75)	(42.90)	(9.74)
$KCo(2,6\text{–}Cl_2C_6H_3O)_3 \cdot THF$*	9.14	5.85	76.18	41.13	11.10
(rose)	(8.98)	(5.96)	(74.08)	(40.28)	(10.81)
$KCo(2,4\text{–}Cl_2C_6H_3O)_3 \cdot 2THF$[b]	8.33	5.46	64.99	41.56	9.61
(blue)	(8.10)	(5.37)	(66.75)	(42.90)	(9.74)
$KCo(2,4\text{–}Cl_2C_6H_3O)_3 \cdot THF$*	8.67	6.00	72.54	38.95	10.75
(rose)	(8.96)	(5.96)	(74.08)	(40.28)	(10.81)
$KCo(m\text{–}ClC_6H_3O)_3 \cdot 2THF$[c]	9.65	6.39	62.48	50.83	5.74
(blue violet cryst).	(9.43)	(6.26)	(61.25)	(49.99)	(5.68)
$KCo(m\text{–}ClC_6H_3O)_3 \cdot THF$*	10.99	7.04	70.11	48.12	6.24
(rose)	(10.66)	(7.07)	(69.23)	(47.87)	(6.42)
$KCo(o\text{–}ClC_6H_3O)_3 \cdot 2THF$[c]	9.15	6.18	62.08	51.03	5.43
(pale blue)	(9.43)	(6.26)	(61.25)	(49.99)	(5.68)
$KCo(o\text{–}ClC_6H_3O)_3 \cdot THF$*	11.02	7.10	68.14	46.42	6.35
(rose)	(10.66)	(7.07)	(69.23)	(47.87)	(6.42)
$KCo(o\text{–}BrC_6H_3O)_3 \cdot 2THF$[c]	7.54	4.99	69.83	42.33	11.17
(blue)	(7.77)	(5.16)	(68.07)	(41.20)	(10.54)
$KCo(o\text{–}BrC_6H_3O)_3 \cdot THF$*	8.92	5.86	74.43	37.32	11.40
(rose)	(8.59)	(5.70)	(75.21)	(38.52)	(11.65)
$KCo(p\text{–}BrC_6H_3O)_3 \cdot THF$**[d]	8.81	5.80	75.57	39.02	11.98
(rose violet)	(8.59)	(5.70)	(75.21)	(38.52)	(11.65)
$KCo(2,4\text{–}(CH_3)_2C_6H_3O)_3 \cdot 2THF$[b]	9.94	6.33	62.93	65.12	—
(dark blue)	(9.73)	(6.46)	(60.03)	(63.47)	
$KCo(2,4\text{–}(CH_3)_3C_6H_3O)_3 \cdot THF$*	10.77	7.12	69.01	64.12	—
(blue)	(11.05)	(7.33)	(68.13)	(63.03)	

(a) Characterization carried out in its THF soln. Corresponded the ratio 1 : 1 : 3 for Co : K : OAr.
(b) Crystallized by addition of n-hexane and cooling for 8 days at –50°C.
(c) Crystallized from its THF solution after 10 days at –78°C.
(d) Crystallized from its THF solution after 15 days at –78°C.
** Decomposed at 130°C/0.8 Torr.

Thermal lability

While, all the outer sphere THF molecules of the sodium-tetra-aroxo-cobaltate(II) complexes splitted at 80–120°C/0.8 Torr[1], only one of the two THF

molecules of the potassium-tri-aroxo-cobaltate(II) complexes splitted at 80–90°C/0.8 Torr, accompanied by changing in the parent colour (mainly to rose), supported by the elemental and analytical analysis of the resulted product, which revealed the formula $KCo(O-C_6H_4-X)_3.THF$ (Table 1). As the temprature raised to 120–130°C/0.8 torr, the second THF molecule splitted out accompanied by decomposition of the complexes, this suggested that the second THF molecule is incorporated in the coordination sphere of Co(II).

The relatively low temperature (120–130°C/0.8 Torr.) at which potassium tri-aroxo-complexes, decomposed (to black resine), suggested the less stability of these complexes (disodium-tetra-aroxo-cobaltate(II) decomposed at 150–160°C/0.8 Torr.). This could be attributed to the electropositivity of the potassium atom.

The *p*-bromo derivative is the only one of these series which contains one THF-molecule in it's structural formula. This is unreasonable and we have no ready explanation for this result, although it decomposed at the same decomposition temperature range of the other complexes.

Electronic and IR spectra

Electronic spectra, were recorded in THF solution. The intense blue colour suggested that they were probably having tetrahedral streochemistry. The two observed bands at 16000–17200 cm^{-1} and 7000 cm^{-1} are assigned to the spin allowed transition $\nu_2(^4A_2 \rightarrow {}^4T_1)(F)$ and $\nu_3(^4A_2 \rightarrow {}^4T_1)(P)$ respectively[9]. The third spin allowed transition $\nu_1(^4A_2 \rightarrow {}^4T_2)$, (10 Dq) were calculated by Tanabe-Sugano equations[10].

Infrared spectra indicated the presence of a broad band at 3480 ± 150 cm^{-1} which is probably to be attributed to this transition.

TABLE 2
MOLAR CONDUCTANCE OF THE COMPLEXES

Complex	Molar Conductance [10^{-3}M] $Ohms^{-1}$	
	THF	DMF
$KCo(o\text{–}NO_2C_6H_4O)_3 \cdot 2THF$	—	26
$KCo(2,6\text{–}Cl_2C_6H_3O)_3 \cdot 2THF$	—	33
$KCo(2,4\text{–}Cl_2C_6H_3O)_3 \cdot 2THF$	—	29
$KCo(m\text{–}ClC_6H_4O)_3 \cdot 2THF$	—	47
$KCo(o\text{–}ClC_6H_4O)_3 \cdot 2THF$	—	45
$KCo(o\text{–}BrC_6H_4O)_3 \cdot 2THF$	—	42
$KCo(p\text{–}BrC_6H_4O)_3 \cdot THF$	—	47
$KCo(2,4\text{–}(CH_3)_2 \cdot C_6H_3O)_3 \cdot 2THF$	1.5	56

The assignment of the IR spectra of the solid complexes are summarized in Table 3.

TABLE 3
INFRARED VIBRATION FREQUENCIES OF KCo(O-⟨⟩-$_x$)$_3$. 2THF COMPLEXES (cm^{-1}).

Complexes		νC–O	νCo–O	νC ⋯ C	$^4T_2 \rightarrow {}^4T_2$	
KCo(2, 6–$Cl_2C_6H_3O)_3$ · 2THF		1168	665		3460	
KCo(2, 4–$Cl_2C_6H_3O)_3$ · 2THF.		1160	670	1600	3480	
KCo(*o*–$ClC_6H_4O)_3$ · 2THF	a	1150	642	1460	3470	10Dq
KCo(*o*–$BrC_6H_4O)_3$ · 2THF	b	1130	618		3465	
KCo(2, 4–$(CH_3)_2$ · $C_6H_4O)_3$ · 2THF		1085	696		3495	

(a) νC–Cl, 780 cm^{-1} (b) νC–Br, 755 cm^{-1}

The weak band at *ca.* 19500 cm^{-1} observed in the visible spectra, could be assigned to the spin-forbidden transition to the doublet state. The spectral data are collected in Table 4.

TABLE 4
ELECTRONIC STRUCTURE PARAMETERS FOR TETRAHEDRAL Co(II) IN KCo(O-⟨⟩-$_x$)$_3$. 2THF. COMPLEXES.

Complex	ν_3 cm^{-1}	ν_2 cm^{-1}	(10Dq) ν_3 cm^{-1}	B_{35} cm^{-1}	β_{35}
KCo(*o*–$NO_2C_6H_4O)_3$ · nTHF	14925	6500	3063	814	0.727
	14750*	6450	3039	806	0.720
KCo(2, 6–$Cl_2C_6H_3O)_3$ · 2THF	16529	6900	3261	909	0.811
KCo(2, 4–$Cl_2C_6H_3O)_3$ · 2THF	16529	6950	3283	908	0.811
	16550*	6900	3260	904	0.807
KCo(*m*–$ClC_6H_4O)_3$ · 2THF	16667	7000	3307	916	0.818
KCo(*o*–$ClC_6H_4O)_3$ · 2THF	16750	7050	3331	920	0.821
	16520*	7050	3327	905	0.808
KCo(*o*–$BrC_6H_4O)_3$ · 2THF	16880	7100	3354	928	0.829
KCo(*p*–$BrC_6H_4O)_3$ · THF	16960	7150	3377	934	0.834
	16700*	7100	3351	916	0.808
KCo(2, 4 · $(CH_3)_2C_6H_4O)_3$ · 2THF	17100	7200	3401	940	0.840

* Recorded in DMF

The values of B_{35} are of the order of 70% of the free ion value, suggesting that, there is an appreciable orbital overlap, which is expected, thus oxygen is a relatively large polarizable atom[2]. On the other hand the values of B_{35} and β_{35} reflected the covalency nature of these complexes, supported by conductance measurements which, showed that all the complexes are essentially non-electrolytes in their THF solutions, only the KCo(O-⟨⟩(-CH_3)-CH_3)$_3$ · 2THF appears to be weak electrolyte (Table 2).

Solvolysis may be occured as the dielectric constants[11] of the solvent increase. Thus the DMF-electronic spectra of these complexes showed a

bathochromic shift of the transition frequency by about 250 cm^{-1} , which consequently affected the calculated values of B_{35} and β_{35} (Table 4). Conductivity data show that potassium-triaroxo-cobaltate(II) complexes behave as weak electrolyte in their DMF solutions. This could be attributed to solvolysis processes. The 10 Dq and B_{35} values are comparable with that found for tetrahedral geometry of Co(II), which also confirm the position of the ArO^- ligand which we have previously fitted[1] in the spectrochemical and nephelauxtic series. Inductive effects (I'S) of the substituents in the phenoxide ring, as we have been already discussed, affected the 10 Dq values.

The slightly lowering; but measureable in the 10 Dq values in comparison with those values of the disodium-tetra-aroxo-cobaltate complexes could be interpreted on the bases of the large atomic size of the potassium atom together with the increasing in the electropositivity on going from sodium to potassium as a bridging atom.

Effect of the atomic size of the bridging atoms on the streochemistry of this type of double metal-aroxides complexes have not been previously discussed.

Magnetic Moment

The magnetic susceptibilities of these complexes (Table 5) fall in the range acceptable for tetrahedral cobalt(II)[10]. One of the interesting features of these data is their harmony with our derived aroxid-spectrochemical series[1]. The higher magnetic moment than the spin only value (3.88 BM), may involve the spin-orbit coupling. The expected magnetic moment (469 ± 0.06 BM) calculated[10] by the aid of the spectral data is in accord with it's measured value.

Spin-Orbit-Coupling

The 20% lowering in spin-orbit coupling constant (Table 5) than the free ion value (−178 cm^{-1}) can be explained in terms of small degree of delocalization of the *d*-orbital[12,13].

TABLE 5
MAGNETIC SUSCEPTIBILITY MEASUREMENTS AT 297 K FOR $KCo(O-C_6H_4-X)_3 \cdot 2THF$ COMPLEXES

Complex	$\chi_{mol} \cdot 10^{-6}$	$\chi^{dia} \cdot 10^{-6}$	$\chi^{corr.}_{mol}$	μ_{exp} (B.M)	$\mu_{calc.}$ (B.M.)	$\lambda\ cm^{-1}$
$KCo(o\text{–}NO_2C_6H_4O)_3 \cdot nTHF$	8972	−355	9308	4.71	4.75	161
$KCo(2,6\text{–}Cl_2C_6H_3O)_3 \cdot 2THF$	8750	−369	9105	4.65	4.70	159
$KCo(2,4\text{–}Cl_2C_6H_3O)_3 \cdot 2THF$	8642	−369	9011	4.63	4.70	156
$KCo(m\text{–}ClC_6H_4O)_3 \cdot 2THF$	8600	−352	8952	4.62	4.62	154
$KCo(o\text{–}ClC_6H_4O)_3 \cdot 2THF$	8519	−352	8871	4.59	4.69	149
$KCo(o\text{–}BrC_6H_4O)_3 \cdot 2THF$	8514	−383	8897	4.60	4.68	152
$KCo(p\text{–}BrC_6H_4O)_3 \cdot THF$	8004	−331	8935	4.61	4.67	155
$KCo(2,4\text{–}(CH_3)_2 \cdot C_6H_3O)_3$ 2THF	8598	−372	8970	4.62	4.67	158

EXPERIMENTAL

Preparation

All glass apparatus with standard joints were used throughout the experiments. Stringent precuations were taken to avoid moisture and atmospheric oxygen. All preparation and subsequent handling of materials were carried out under dry argon.

Solvents were dried over sodium and benzophenone and distilled immediatly prior to use. Anhydrous $CoBr_2$ were prepared by literature method[14]. Alkali metal aroxides were prepared by the reaction of the potassium metal with the the corresponding phenol derivatives using THF as a solvent[4].

The electronic spectra were recorded in THF and DMF using carry 14-spectrophotometer. IR-spectra were recorded on Perkin-Elmener 598-spectrophotometer using CsI. The magnetic susceptibility was measured by Gouy method.

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