On the Optically Active Anion Tris(2-sulfonatoethylxanthogenato)-cobaltate(III)

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Tripotassium tris(O-(2-sulfonatoethyl)dithiocarbonato-S,S)cobaltate(III), $K_3[Co(S_2COC_2H_5SO_3)_3]$.$2H_2O$, has been resolved. The absorption, circular dichroism, and magneto-circular dichroism spectra of this complex, of tris(O-ethyldithiocarbonato-S,S)-indium(III), and of the xanthogenate ligand have been measured in the visible and UV spectral region. Application of exciton theory shows that the $(+)_{538}$-isomer of the cobaltate complex has the absolute configuration Δ.

This paper reports on the complete resolution of the tris(xanthogenato)cobaltate(III) complex where the optically inactive ligand is the xanthogenate of potassium 2-hydroxyethansulfonate. The absorption (ABS), circular dichroism (CD) and magneto-circular dichroism (MCD) spectra of this complex are compared with the ABS and MCD of tris-(ethylxanthogenato)indium(III) and of the ligand, potassium ethylxanthogenate.

In 1954 Krebs and Rasche[1] achieved a partial resolution of the potassium salt of tris(O-(2-sulfonato-ethyl)dithiocarbonato)cobaltate(III) by passing an aqueous solution through a column packed with 10 cm of dry potato starch. (Being a xanthogenate of isethionic acid, the abbreviation isx will be used for this ligand). We have prepared the catoptric forms by precipitation of the diastereoisomer with the optically active 1-phenylethylamine.HCl, and also by separation of the racemate on a column packed with a crosslinked dextran. The column separation was carried out in 10 days at 5 °C, where the half-life[2] for racemization is 2 months. Combination of the two ways of resolution gives

the pure isomers whose optical activity, determined as the ratio of $\Delta\varepsilon$ at 630 nm to ε at 621 nm, is $\pm 3.98 \times 10^{-2}$.

EXPERIMENTAL

Dipotassium O-(2-sulfonatoethyl)dithiocarbonate was prepared as described by Krebs and Rasche[1] by shaking equimolar amounts of potassium 2-hydroxyethansulfonate, potassium hydroxide, and carbon disulfide in water for a week. After recrystallization from methanol – water (1:1) a mixture of the xanthogenate and the starting alcohol was obtained.

Tripotassium tris(O-(2-sulfonatoethyl)dithiocarbonato)cobaltate(III), $K_3[Co(S_2COC_2H_4SO_3)_3]$.$2H_2O$ ($K_3[Co isx_3]$.2 aq) : 60 g of the xanthogenate-alcohol mixture containing 30 g (0.11 mol) of K_2isx, was dissolved in 100 ml of water, cooled on ice, and added dropwise to a well-stirred, cooled solution of 6.2 g (26 mmol) hexaaquacobalt(II) chloride, 10 ml (175 mmol) of glacial acetic acid, and 10 ml 9.8 M hydrogen peroxide in 10 ml of water. The green complex was precipitated with 650 ml of methanol and recrystallized from 20 ml of water. Yield: 10 g (47 %). Analysis: C, H, S, Co, thermogravimetric determination of water.

R(+) and S(−) 1-Phenylethylammonium chloride was prepared according to the literature.[3,4]

Resolution of the tris(2-sulfonatoethylxanthogenato)cobaltate(III) ion. Chromatography. Two columns, 25 mm × 900 mm, were packed with the crosslinked dextran "Sephadex G-25, superfine" suspended in 0.01 M hydrochloric acid. The columns were provided with capillary tubes so that the outlet of one column could be connected to the

inlet of the other one, keeping the volume between the columns at *ca.* 3 ml. The columns were operated at 5 °C in order to prevent racemization during the separation. 500 mg of the complex $K_3[Co$ isx$_3$].2 aq was dissolved in 2.5 ml 0.01 M hydrochloric acid, sorbed on one of the columns and eluted with 0.01 M hydrochloric acid. Having passed the first column the main component was transferred to the second column, whereas five small components were discarded. The main component was allowed to pass each column twice (360 cm, 10 days) and was then collected in 50 fractions of 5 ml. The values of $\Delta\varepsilon(630$ nm)$/\varepsilon(621$ nm) decreased smoothly from $+3.86 \times 10^{-2}$ (fraction 1) through 0 (fraction 15) to -1×10^{-2} (fraction 40−50).

Precipitation of diastereoisomers. 3.9 g (25 mmol) of (−)-1-phenylethylammonium chloride dissolved in 3 ml of methanol-water (1:1) was added to a solution of 2.0 g (2.5 mmol) of the racemic $K_3[Co$ isx$_3$].2aq in 24 ml of methanol-water (1:1) and left at −17 °C. The crystalline material ($\Delta\varepsilon(630$ nm)$/\varepsilon(621$ nm)$\approx -1.5 \times 10^{-2}$) which separated was recrystallized twice from the minimum amount of methanol-water at room temperature, adding each time further amine hydrochloride and cooling to −17 °C. The precipitate thus obtained ($\Delta\varepsilon(630$ nm)$/\varepsilon(621$ nm)$\approx -3.5 \times 10^{-2}$) was recrystallized twice from methanol-water in the same way except for the addition of the amine hydrochloride. The complex was then converted to the potassium salt on a column (15 mm × 145 mm) packed with Sephadex anion exchanger QAE-A 25 and eluted with 2 M potassium chloride. The complex is slightly soluble in saturated potassium chloride. Therefore, the eluate (200 ml) was evaporated to dryness (vacuum, 20 °C), 90 ml of water was added to dissolve the potassium chloride, further 9 ml of water was added and the solution was filtered. 300 ml of methanol was added to the mother liquor to precipitate *ca.* 80 % of the potassium chloride which was removed. By evaporation of the filtrate, adding 20 ml+2 ml of water, a further small amount of the complex was obtained. Yield: 20 mg (2.5×10^{-5} mol, 2 %) of $(−)_{538}K_3[Co(S_2COC_2H_4SO_3)_3].2H_2O$ with the activity $\Delta\varepsilon(630$ nm)$/\varepsilon(621$ nm)$= -3.88 \times 10^{-2}$.

Combination of the methods. 150 mg of $(+)K_3$-$[Co$ isx$_3$].2aq prepared by precipitation using (+) amine hydrochloride, was dissolved in 0.8 ml 0.01 M hydrochloric acid and separated on the column. The fractions Nos. 2−7 off the column all showed the ratio $\Delta\varepsilon(630$ nm)$/\varepsilon(621$ nm)$= +3.98 \times 10^{-2}$. This figure is obtained in water as well as in 0.01 M hydrochloric acid.

Resolution on potato starch. A repetition of Krebs and Rasche's experiment[1] gave $\Delta\varepsilon(630$ nm)$/\varepsilon(621$ nm)$= -2.3 \times 10^{-3}$ for fraction No. 1 and $+4.6 \times$
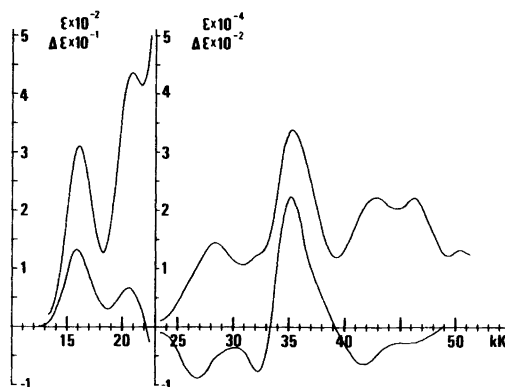

Fig. 1. Absorption (upper curve) and circular dichroism (lower curve) spectra of aqueous solutions of $(+)_{538}K_3[Co(S_2COC_2H_4SO_3)_3].2H_2O$ at *ca.* 300 K. $\Delta\varepsilon(630$ nm)$/\varepsilon(621$ nm)$= +3.98 \times 10^{-2}$.

10^{-3} for fraction No. 9 off the column.

Potassium O-ethyldithiocarbonate (K etx) was obtained from Fluka AG (*puriss.*).

Tris(O-ethyldithiocarbonato)indium(III), In-$(S_2COC_2H_5)_3$ (In etx$_3$), was prepared by F. Galsbøl.[5]

Absorption and circular dichroism spectra. The room temperature spectra were measured using a Cary 14 Spectrophotometer and a Jouan Dichrographe 2 B. The low temperature spectra were measured on 96 % ethanol−methanol (5:1) glasses at *ca.* 110 K as previously described.[6]

$K_3[Co$ isx$_3$].2aq: The ABS and CD spectra at 300 K were measured on aqueous solutions: Fig. 1,
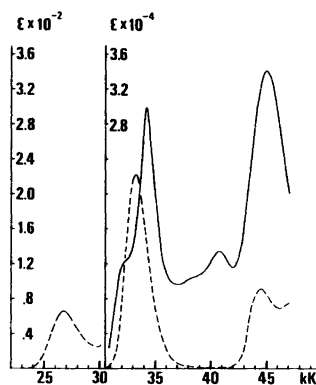

Fig. 2. Absorption spectra of In(S$_2$COC$_2$H$_5$)$_3$ (———) and of KS$_2$COC$_2$H$_5$ (−−−) in 96 % ethanol−methanol at *ca.* 110 K.

Table 1. Data for absorption and circular-dichroism spectra. A and D: $(+)_{538}K_3[Co(S_2COC_2H_4SO_3)_3]$.- $2H_2O$. B and E: $In(S_2COC_2H_5)_3$. C and F: $KS_2COC_2H_5$. A, B, C are measured at *ca.* 300 K, D, E, F at *ca.* 110 K. Owing to the contraction by cooling, the molar absorptivities ε are relative figures for D, E and F. Units for v are 10^3 cm^{-1}, $\Delta\varepsilon = \varepsilon_l - \varepsilon_r$.

A, ABS[a]		A, CD[a]		B, ABS[b]		C, ABS[b]		D, ABS[b]		E, ABS[b]		F, ABS[b]	
v	(ε)	v	$(\Delta\varepsilon)$	v	(ε)	v	(ε)	v	(ε)	v	(ε)	v	(ε)
16.10	(326)	15.87	(+13)										
20.9	(451)	20.6	(+7)										
28.4	(14100)	26.7	(−88)			26.0	(57)	28.3	(20700)			28.8	(66)
32	(sh)	32.2	(−76)	31.6	(7800)	32.9	(17700)	32.5	(17400)	32	(sh)	33.2	(22200)
35.4	(33800)	35.2	(+224)	34.1	(20300)			35.3	(46600)	34.2	(29900)		
										38.3	(sh)		
										40.8	(13500)		
42.7	(25000)	41.7	(−63)	44.6	(41400)	44.2	(9000)	43.3	(29300)	44.9	(34100)	44.5	(9200)
46.3	(25000)	46.1	(−27)										
50.4	(13400)												

[a] Measured in aqueous solution. [b] Measured in 96 % ethanol − methanol (5:1).

Table 1. The UV spectrum in alcoholic solution is identical to that in aqueous solution. At 110 K the peak (ABS) at 32.5 kK is clearly separated from the adjacent peak at 35.3 kK.

[In etx$_3$]: The ABS spectrum was measured in alcoholic solution. At 300 K the peak at 31.6 kK is clearly separated from the adjacent one at 34.1 kK, whereas the peak at *ca.* 41 kK is hidden. The spectrum at 110 K is shown in Fig. 2. K$_2$ isx and K etx have virtually identical spectra and those of K etx at 110 K are shown in Fig. 2.

Magneto-circular dichroism spectra were measured at room temperature using a Jouan-Russel Dichrographe III equipped with an electromagnet, 1 T. The data for K$_3$[Co isx$_3$].2aq and [In etx$_3$] are given in Table 2. No MCD was detected in aqueous solutions of K etx within a detection limit of *ca.* $\Delta\varepsilon/\varepsilon = 5 \times 10^{-6}$.

Table 2. Magneto-circular dichroism. A: $K_3[Co(S_2COC_2H_4SO_3)_3].2H_2O$ in aqueous solution. B: $In(S_2COC_2H_5)_3$ in 96 % ethanol. The values of $\Delta\varepsilon = \varepsilon_l - \varepsilon_r$ are given for a magnetic field of 1 T and parallel to the direction of propagation of the light.

A				B			
ABS	MCD			ABS	MCD		
v	v	$(\Delta\varepsilon)$	Class[a]	v	v	$(\Delta\varepsilon)$	Class[a]
16.10	~16.5	(−0.003)	B				
20.9	~20.5	(−0.004)	B				
28.4	25	(+0.3)	A				
	28	(−0.3)					
32	34	(+0.6)	B	31.6		no MCD	
35.4	37	(−0.6)	B	34.1		no MCD	
					40	(−1)	A
					>42	(?)	
42.7	41	(−0.3)	B				
				44.6		MCD not determined	
46.3	MCD not determined						

[a] The symbols A and B refer to the common classification[7] of MCD-spectra.

Table 3. Tentative assignments of the observed electronic transitions. The energy of a transition is given, followed by a symmetry description of the molecular orbitals involved.

$C_3H_5OCS_2^-$	$In(S_2COC_2H_5)_3$	$Co(S_2COC_2H_4SO_3)_3^{3-}$
		16 kK; $^1A_1 \rightarrow {}^1T_1$ (O); ligand field
		21 kK; $^1A_1 \rightarrow {}^1T_2$ (O); ligand field
26 kK; $n \rightarrow \pi^*$		28 kK; $^1A_1 \rightarrow {}^1T_1$ (O); $4s,n \rightarrow 4p,\pi^*$
	32 kK; $^1A_1 \rightarrow {}^1E$ (D_3); exciton, $\pi \rightarrow \pi^*$	32 kK; $^1A_1 \rightarrow {}^1E$ (D_3); exciton, $\pi \rightarrow \pi^*$
33 kK; $\pi \rightarrow \pi^*$	34 kK; $^1A_1 \rightarrow {}^1A_2$ (D_3); exciton, $\pi \rightarrow \pi^*$	35 kK; $^1A_1 \rightarrow {}^1A_2$($D_3$); exciton, $\pi \rightarrow \pi^*$
	41 kK; $^1A_1 \rightarrow {}^1T_1$ (O); $5s,n \rightarrow 5p,\pi^*$	
44 kK; $\pi \rightarrow \pi^*$	45 kK; $^1A_1 \rightarrow {}^1T_2$ (O); $\pi \rightarrow \pi^*$	43 kK, 46 kK; $\pi \rightarrow \pi^*$ and ligand(π)$\rightarrow$metal(e)

DISCUSSION

In this section the experimental facts will be interpreted in a qualitative way with emphasis on symmetry arguments. We have in Table 3 brought forward for discussion an assignment of the observed electronic transitions.

The transitions in the free xanthogenate ion can be identified by comparison with the similar *N,N*-dialkyldithiocarbaminate ions.[8] Both chromophores $-OCS_2^-$ and $>NCS_2^-$ are planar, and semiempirical MO calculations on the π-electron system of the latter ion show that the electric transition dipole moment in the lowest energy transition, $n \rightarrow \pi^*$, is polarized perpendicular to the plane, whereas the $\pi - \pi^*$ transitions are polarized in the plane. The lower energy $\pi \rightarrow \pi^*$ transition is polarized in the sulfur to sulfur direction and the higher energy one is polarized perpendicular to this direction. Here, n is an in-plane non-bonding sulfur orbital and the $n \rightarrow \pi^*$ transition is almost forbidden.

The ligand $n \rightarrow \pi^*$ transition can be identified in the complexes. In both complexes the symmetry of the ground-state is $^1A_1$ and in octahedral symmetry the electric dipole transitions of the ligands couple to give exciton transitions[9] of the symmetry $^1A_1 \rightarrow {}^1T_1$. However, to some extent the n orbitals will mix with the $4s$ orbital on cobalt or the $5s$ orbital on indium, and similarly, but probably to a lesser extent, the π^* orbitals will mix with the $4p$ or the $5p$ orbitals on the metals. This is expected to give rise to a blue shift of the transition, and in agreement with the fact that the $5s$ orbital on an energy scale is closer to the n orbitals than is the $4s$ orbital,[10] the transition is found at 41 kK in the indium complex and at 28 kK in the cobalt complex. We note that the MCD spectra support this identification, since no MCD is found in the ligand and an A-type MCD arising from the inter-

mixing of the metal s and p orbitals is observed in the complexes.

Upon complex formation the 33 kK $\pi \rightarrow \pi^*$ transition of the ligands is expected to give an appreciable exciton coupling.[9] Therefore, since the actual symmetry of the complexes is D_3, the transition $^1A_1 \rightarrow {}^1T_1$ (octahedral description) will split into the transitions $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_2$ of different energy. For such cases it has been shown[9] that the relation $2D(^1A_1 \rightarrow {}^1E) = D(^1A_1 \rightarrow {}^1A_2)$ holds true for the dipole strengths and that $R(^1A_1 \rightarrow {}^1E) = -R^1A_1 \rightarrow {}^1A_2)$ holds true for the rotatory strengths. From this, the assignments in Table 3 follow. Further, since $R(^1A_1 \rightarrow {}^1A_2) > 0$ for the $(+)_{538}$tris(2-sulfonatoethylxanthogenato)cobaltate-(III) ion shown in Fig. 1, this isomer has the absolute configuration Δ. Finally, the MCD spectra show that the intermixing of metal and ligand orbitals takes place to a greater extent in the cobalt complex than in the indium complex.

The exciton coupling of the 44 kK $\pi \rightarrow \pi^*$ transition is not expected to yield circular dichroism. The fact that CD is observed in the cobalt complex is taken as an indication of the mixing of metal and ligand orbitals. Also, we have no means to differentiate between this transition and the ligand to metal (empty e orbitals) charge-transfer transition in this spectral region.

The ligand field transitions in the cobalt complex have been assigned in the usual manner.[11]

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