

Spontaneous Resolution and Polymorphism of Potassium Tris(oxalato)cobaltate(III). X-ray Crystallographic and Thermal Studies¹

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Abstract: The spontaneous resolution of potassium tris(oxalato)cobaltate(III), $K_3[Co(ox)_3] \cdot nH_2O$, reported by Jaeger in 1919, has been reinvestigated. The existence of two kinds of racemic crystals, racemic A (dihydrate) and racemic B (3.5 hydrate), was demonstrated. The conditions which control the deposition of these crystals (racemic A, racemic B, and optically active crystals) are very complicated, and the crystallization temperature previously mentioned by Jaeger does not have a definitive meaning. The inconsistency of previous reports on the thermal behavior of the "racemic" compound can be interpreted as arising from samples containing a mixture of racemic-A and racemic-B crystals. The crystal structures of these three compounds have been determined by single-crystal X-ray diffraction technique. Crystal data are as follows: racemic A, $K_3[Co(ox)_3] \cdot 2H_2O$, monoclinic, $a = 23.658$ (6) Å, $b = 11.323$ (3) Å, $c = 12.557$ (4) Å, $\beta = 117.50$ (2)°, space group $C2/c$, $Z = 8$, $R = 0.036$, 3052 reflections; racemic B, $K_3[Co(ox)_3] \cdot 3.5H_2O$, triclinic, $a = 14.957$ (6) Å, $b = 14.659$ (6) Å, $c = 8.427$ (2) Å, $\alpha = 94.55$ (3)°, $\beta = 82.85$ (3)°, $\gamma = 61.60$ (3)°, space group $P\bar{1}$, $Z = 4$, $R = 0.051$, 6748 reflections; optically active crystal, Δ - $K_3[Co(ox)_3] \cdot 2H_2O$, trigonal, $a = 11.258$ (6) Å, $c = 20.291$ (7) Å, space group $P3_121$, $Z = 6$, $R = 0.051$, 1677 reflections. In the optically active crystal, the complex anions form a three-dimensional network including a double spiral chainlike structure, while in the racemic-B crystal they form a one-dimensional zigzag chain. The packing modes of the complex anion and the potassium cation in those three crystals are compared, and the enantiomeric discrimination in favor of the spontaneously resolvable structure is analyzed.

Spontaneous optical resolution on crystallization is one of the most fascinating phenomena in nature. Since Pasteur discovered the first example of it on sodium ammonium tartrate tetrahydrate in 1850,² several hundred examples of spontaneously resolved compounds have been reported.³

Potassium tris(oxalato)cobaltate(III), $K_3[Co(ox)_3] \cdot nH_2O$, where $ox = (C_2O_4)^{2-}$, reported by Jaeger in 1919 was the first example involving a metal complex. He stated that optically active crystals were obtained at 13.2 °C or above while racemic ones were deposited below this temperature.⁴ The reproducibility of his experiment, however, was later doubted by Gillard et al.⁵ and Wolf.⁶ Moreover, many discrepancies were found between Jaeger's data and those of the later studies. For example, he reported that the optically active crystal was monohydrated and isomorphous with the corresponding rhodium(III) salt, but Herpin suggested that the salt was dihydrated.⁷ Likewise, Brady et al.⁸ reported that it was 2.6 hydrated in their pressure-effect study.

For the racemic crystal, Jaeger reported that it was 3.5 hydrated and triclinic, but Gillard stated that it was 3.5 hydrated and monoclinic.^{4,5} The thermal analyses studies by Wendlandt,⁹ Nagase,¹⁰ and Tanaka¹¹ showed that racemic $K_3[Co(ox)_3] \cdot nH_2O$ contains three water molecules.

We carefully reinvestigated the crystallization of this compound over a wide range of temperatures and found that two kinds of racemic crystals (dihydrate and 3.5 hydrate) and a pair of spontaneously resolved optically active crystals (dihydrate), which could be separated manually, could be obtained from the racemic solution. Using these single crystals, we performed X-ray structure

determinations to gain insight into the origin of the spontaneous resolution of this compound. The thermal behavior of these crystals was also reinvestigated.

Experimental Section

Crystallization of the Compounds. The complex $K_3[Co(ox)_3] \cdot nH_2O$ was prepared according to the literature, and elemental analyses gave reasonable results.¹² Crystallization was carried out in the dark at several temperatures over the range 5–30 °C from saturated racemic aqueous solutions and regulated within ± 0.1 °C and in the absence of light.

Three kinds of crystals were obtained (racemic A, I, racemic B, II, and optically active, III, crystals), which could be distinguished by inspection of the crystal shape under a microscope and by differential scanning calorimetric (DSC) measurements.¹³

TG Measurement. Thermogravimetric (TG) curves were obtained with a Shinku-Riko TGD-3000 RH-N thermobalance in a dynamic nitrogen atmosphere (40 mL/min). A powdered sample (typically 4.3–4.7 mg) in an aluminum crucible was used in each measurement. The heating rate was approximately linear with time at 5 °C/min from room temperature (25 °C) to 400 °C.

DSC Measurement. DSC curves were obtained with a Rigaku 8055-C-1 standard differential scanning calorimeter in a dynamic nitrogen atmosphere (25 mL/min). About 7 mg of powdered sample was used in each measurement. The heating rate was approximately linear with time at about 10 °C/min from room temperature (25 °C) to 300 °C.

Water of Crystallization. The number of water molecules of crystallization was determined coulometrically by using a Hiranuma AQ-3 Aquacounter. About 10 mg of a powdered sample was used in each measurement. The values obtained are 2.01, 3.53, and 2.10 for I, II, and III, respectively.

CD Measurement. CD curves were obtained with a JASCO J-40CS recording spectropolarimeter at room temperature.

X-ray Measurement. The cell dimensions and space group symmetries were preliminarily checked by Weissenberg photographs by using Ni K_α radiation. The systematic absences suggested the following possible space groups: $C2/c$ or Cc for racemic, $K_3[Co(ox)_3] \cdot 2H_2O$, I; $P\bar{1}$ or $P\bar{1}$ for racemic B, $K_3[Co(ox)_3] \cdot 3.5H_2O$, II; $P3_121$ or $P3_221$ for optically active crystals, Δ (or Δ)- $K_3[Co(ox)_3] \cdot 2H_2O$, III. Statistical analyses of intensities indicated space groups $C2/c$ and $P\bar{1}$ for I and II, respectively. The

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(12) Palmer, W. G. "Experimental Inorganic Chemistry"; Cambridge University Press: London, 1962; p 550. The value 3.0 for waters of crystallization represents an average for our samples used (C: found $14.3 \pm 3\%$, calcd 14.58% for $K_3[Co(C_2O_4)_3] \cdot 3H_2O$).

(13) DSC curves of the three kinds of crystals (I, II, and III) are different enough to distinguish among their crystal forms.

Table I. Crystal Forms Obtained at Several Temperatures

temp, °C	rac-A	rac-B	optically active
	I	II	III
5.0 ^a	o ^b	o	x
10.0	o	o	?
13.2 ^c	o	o	o
15.0	o	o	o
20.0	?	o	o
22.0	?	o	o
25.0	x	o	o
30.0	?	o	o

^a Temperature accuracy ± 0.1 °C. ^b The o, x, and ? marks indicate the following results: (o) this form was obtained; (x) this form was not obtained; (?) within 10 independent runs, this form was obtained in 2 or 3 times. ^c Jaeger reported that above this temperature, optically active crystals were obtained, while below this temperature racemic crystals were obtained.

space group $P3_121$ was chosen arbitrary for the Δ form of III. The later success of the structure determinations, including the anomalous dispersion correction for III, confirmed these selections.¹⁴ Determination of cell constants and collection of intensity data were carried out on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.7107$ Å). Unit cell constants were determined by least-squares refinement of 18 reflections for each compound. Intensity data were collected by an $\omega - 2\theta$ scan mode up to $2\theta = 55^\circ$ with the scan rate of 16 deg/min (50 kV, 170 mA). The ω scan range was $1.0 + 0.45 \tan \theta$ (deg). Standard LP corrections were applied, but corrections for the absorption effect were neglected ($\mu(\text{Mo } K_\alpha) = 20.9, 19.7, \text{ and } 21.0 \text{ cm}^{-1}$ for I, II, and III). The number of reflections ($F_o > 3\sigma F_o$) are 3052, 6748, and 1677 for I, II, and III, respectively.

Determination and Refinement of the Structures. The structure of each compound was solved by the heavy-atom method. All the non-hydrogen atoms were refined anisotropically. Subsequent difference Fourier maps did not reveal the positions of hydrogen atoms because the thermal vibration of the water molecules was large. For crystal II, the occupancy factors of the disordered water molecules OW(7) and OW(7*), which are 0.5, were estimated from difference maps.

The largest peak in a final difference map was ca. $1.1 \text{ e } \text{Å}^{-3}$ for each compound. The final anisotropic thermal parameters and the listing of observed and calculated structure factors are available as supplementary material. All the atomic scattering factors were taken from Cromer and Waber.¹⁵ The anomalous dispersion coefficients of Cromer and Liberman were used for Co and K atoms.¹⁶ Block-diagonal least-squares refinement to the minimized function $w(F_o - k|F_c|)^2$ was employed. The weights w were taken as $(\sigma^2 + aF_o + bF_o^2)^{-1}$, where σ is the standard deviation for each reflection and the values of a and b used were 0.2 and 0.009, respectively. All the computations were carried out on a HITAC computer at the Hiroshima University Information Processing Center. The computer programs used were UNICS with a slight modification.¹⁷ An ORTEP drawing was carried out by the XTL system on a SYNTEX diffractometer.¹⁸

Results and Discussion

Crystallization of the Compounds. In order to check the reproducibility of Jaeger's experiment, the crystallization of $\text{rac-K}_3[\text{Co}(\text{ox})_3] \cdot n\text{H}_2\text{O}$ ($n = 3$) from the saturated aqueous solutions at several temperatures was reexamined. The results are summarized in Table I. To our surprise, three kinds of crystals were obtained. Below 5 °C, the optically active crystals were not deposited, and at higher temperature (above 20 °C) the racemic-A, I, crystals were difficult to obtain. The racemic-B, II, crystals were deposited at all temperatures in the range. At 13.2 °C, the key temperature that Jaeger reported for spontaneous resolution,

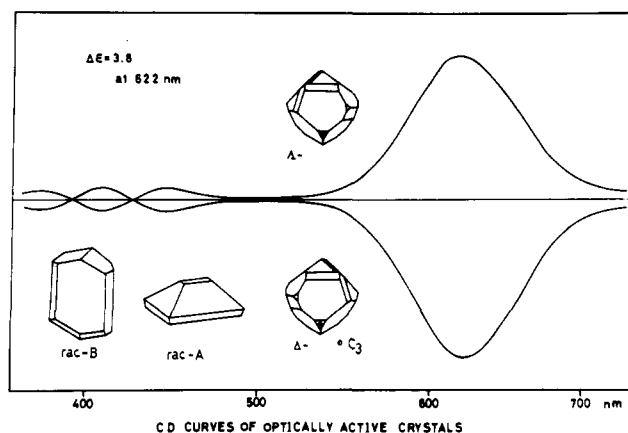
(14) Present crystal structure analysis reveals that space group $P3_121$ corresponds to the Δ isomer and space group $P3_221$ corresponds to the Λ isomer from the anomalous dispersion technique; $R = 0.051$ for $P3_121$ and 0.061 for $P3_221$. The Δ -absolute configuration obtained here agrees well with that reported by Butler and Snow (ref 19).

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**Figure 1.** Enantiomeric pairs of optically active $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 2\text{H}_2\text{O}$ crystals with their CD curves and the sketches of racemic-A and racemic-B crystals.**Table II.** Temperature Range and Mass Loss of Three Kinds of Crystals

temp range, °C	mass loss (obsd), %	mass loss (calcd for the evolution of)
I. Racemic $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 2\text{H}_2\text{O}$ (Monoclinic Form)		
25-95	3.8	3.8 (H_2O)
95-190	8.4	8.4 ($\text{H}_2\text{O} + 0.5\text{CO}_2$)
190-235	2.9	2.9 (0.5CO)
235-285		
285-385	18.2	18.5 (2CO_2)
II. Racemic $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 3.5\text{H}_2\text{O}$ (Triclinic Form)		
25-100	10.8	10.7 ($3\text{H}_2\text{O}$)
100-130	1.8	1.8 ($0.5\text{H}_2\text{O}$)
130-155	4.2	4.4 (0.5CO_2)
155-235	2.8	2.8 (0.5CO)
235-285		
285-390	17.6	17.5 (2CO_2)
III. Active $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 2\text{H}_2\text{O}$ (Trigonal Form)		
25-85	3.7	3.8 (H_2O)
85-138	3.8	3.8 (H_2O)
138-155	4.6	4.6 (0.5CO_2)
155-230	3.0	2.9 (0.5CO)
230-285		
285-385	18.7	18.5 (2CO_2)

all three crystal forms were deposited. It is interesting to note that in most cases, only one kind of crystal was deposited dominantly and that in a few cases two or three kinds of crystals were obtained simultaneously in nearly equal amounts. The conditions which control the deposition of these crystals are complicated, probably due to unavoidable partial decomposition of the $[\text{Co}(\text{ox})_3]^{3-}$ anion.

All discrepancies among the previously reported experimental results could be explained successfully: Jaeger obtained the racemic-B, II, and optically active, III, crystals, and Gillard obtained monoclinic racemic-A, I, crystals.^{4,5}

Though Jaeger reported that the optical resolution of III by the crystal selection method was unsuccessful (confirmed by Gillard and Wolf), we succeeded in obtaining large crystals as shown in Figure 1 ($0.5 \times 0.5 \times 0.4 \text{ cm}^3$) and in separating the enantiomeric pairs of III by a hand-picked method. The CD curves of enantiomeric crystals and the crystal shapes of I (rac-A) and II (rac-B) are also shown in Figure 1.

Thermal Behavior. The TG curves of three kinds of crystals are shown in Figure 2 (supplementary material). The temperature range and the percentage of weight loss are summarized in Table II. The common features are that water molecules are lost first followed by the evolution of CO_2 and CO . No weight loss was observed between 235 and 290 °C and CO_2 loss above 290 °C.

The DSC curves are shown in Figure 3. The endothermic peaks from room temperature to about 120 °C for the three samples correspond to the loss of water molecules. A color change from

Table III. Summary of Crystal Data and Refinements Conditions for Three Kinds of Crystals

	<i>rac</i> -K ₃ [Co(ox) ₃]·2H ₂ O (monoclinic form), I	<i>rac</i> -K ₃ [Co(ox) ₃]·3.5H ₂ O (triclinic form), II	Λ-K ₃ [Co(ox) ₃]·2H ₂ O (trigonal form), III
space group	C2/c	P $\bar{1}$	P3 ₁ 21 (hexagonal set.)
Z	8	4	6
cell dimension			
a, Å	23.658 (6)	14.957 (6)	11.258 (6)
b, Å	11.323 (3)	14.659 (6)	=a
c, Å	12.557 (4)	8.427 (2)	20.291 (7)
α, deg		94.55 (3)	
β, deg	117.50 (2) ^a	82.85 (3)	
γ		61.60 (3)	
vol, Å ³	2984 (2)	1592 (2)	2228 (2)
volume/Z, Å ³	373	398	371
V*, Å ³	332 ^a	326	330
density (obsd), g/cm ³	2.10	2.10	2.11
(calcd), g/cm ³	2.12	2.10	2.13
cryst dimension, mm ³	0.51 × 0.49 × 0.50	0.28 × 0.32 × 0.55	0.52 × 0.46 × 0.48
no. of unique reflect	3602 (2θ < 55°, Mo Kα)	7857 (2θ < 55°, Mo Kα)	2201 (2θ < 55°, Mo Kα)
no. of ref with F _o > 3σ(F _o)	3052	6748	1677
final R ₁ , %	3.6 ^b	5.1	5.1
final R ₂ , %	5.8 ^c	7.6	6.8

^a Effective volume for K₃[Co(ox)₃]; V* = [(volume/Z) - (n20.6)], where 20.6 Å³ is the estimated volume of water molecule. (Harata, K. *Bull. Chem. Soc. Jpn.* 1976, 49, 2066). ^b R₁ = Σ(|F_o| - |F_c|) / Σ|F_o|. ^c R₂ = [Σw(|F_o| - |F_c|)² / Σw(F_o)²]^{1/2}.

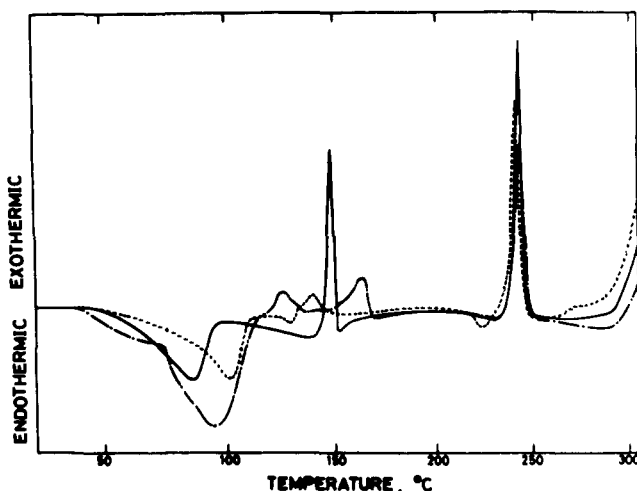


Figure 3. DSC curves of racemic-A I (---), racemic-B II (-·-), and optically active III (—) crystals.

green to reddish-violet, which corresponds to the change in the oxidation state from Co(III) to Co(II), is observed at 150–160 °C for II and III and at 135–145 °C for I. Thus, in II and III, the reduction to the Co(II) state seems to occur concurrently with the evolution of CO₂, but in I it is not so clear.

The TG, DTA, and DSC of the so-called "racemic trihydrate" salt were studied by several authors. There were some discrepancies among these data. Now we can explain these data clearly. The TG and DTA curves by Wendlandt et al.⁹ are close to those of I. Likewise, the TG and DSC curves by Nagase¹⁰ are parallel to those of II. The TG curve by Nanjo et al.¹¹ is different from either of these two, and it can be explained by a mixture of I and II in nearly equal ratio. Thus, all previous data can be interpreted as arising from samples containing I and II in different ratios.

Description of the Crystal Structures. The crystallographic data and structure refinement conditions are summarized in Table III. The final atomic parameters are given in Tables IV, V, and VI. The unit cell packing in I, II, and III are illustrated in Figures 4, 5, and 6 (supplementary material). The numbering scheme of the complex anion in II is shown in Figure 7. Those in I and III also follow the same scheme. Selected bond distances and bond angles are listed in Table VII, and selected interatomic distances and the least-squares planes are listed in Tables VIII and IX, respectively (with supplementary material Tables S-8 and S-9).

All the structures contain discrete [Co(ox)₃]³⁻ anions, potassium cations, and water molecules. In II, there are two crystallographically independent complex anions involving Co(1) and Co(2)

Table IV. Final Atomic Parameters for K₃[Co(ox)₃]·2H₂O (Racemic-A Crystal) I^a

atom	x	y	z	B(av)
Co	0.109 56 (2)	0.234 98 (3)	0.176 81 (3)	1.78
K(1)	0.0	0.083 99 (8)	0.25	2.30
K(2)	0.5	0.164 47 (9)	0.25	3.84
K(3)	0.274 03 (4)	0.053 18 (9)	0.151 10 (8)	3.64
K(4)	0.387 58 (3)	0.227 18 (6)	0.454 78 (6)	2.43
O(1)	0.132 1 (1)	0.396 8 (2)	0.201 5 (2)	2.47
O(2)	0.025 1 (1)	0.286 1 (2)	0.134 3 (2)	2.22
O(3)	0.093 1 (1)	0.243 5 (2)	0.014 3 (2)	2.86
O(4)	0.085 0 (1)	0.074 9 (2)	0.146 9 (2)	2.25
O(5)	0.194 8 (1)	0.188 4 (2)	0.223 5 (2)	2.77
O(6)	0.129 1 (1)	0.212 8 (2)	0.340 4 (2)	2.32
O(7)	0.088 0 (1)	0.572 1 (2)	0.190 8 (2)	2.98
O(8)	-0.029 4 (1)	0.453 2 (2)	0.108 2 (2)	2.67
O(9)	0.070 3 (2)	0.124 0 (3)	-0.139 7 (2)	4.03
O(10)	0.061 3 (1)	-0.058 5 (2)	0.002 5 (2)	2.78
O(11)	0.275 7 (1)	0.104 5 (2)	0.376 9 (3)	3.35
O(12)	0.204 3 (1)	0.128 9 (3)	0.504 4 (2)	3.63
C(1)	0.084 3 (1)	0.464 1 (3)	0.178 8 (3)	2.09
C(2)	0.020 4 (1)	0.399 6 (3)	0.136 5 (3)	1.94
C(3)	0.079 6 (1)	0.141 8 (3)	-0.037 5 (3)	2.40
C(4)	0.074 5 (1)	0.041 6 (3)	0.041 6 (3)	2.07
C(5)	0.222 7 (1)	0.149 3 (3)	0.331 1 (3)	2.38
C(6)	0.184 3 (1)	0.162 0 (3)	0.401 0 (3)	2.42
OW(1)	0.325 6 (2)	0.312 9 (5)	0.216 9 (4)	7.85
OW(2)	0.200 7 (2)	0.381 9 (3)	0.026 4 (4)	6.19

^a Occupancy factors for K(1) and K(2) are 0.5. In the table of atomic parameters, standard deviations on the last significant digits are given in parentheses. Anisotropic thermal parameters are listed in Table S-4 (supplementary material). B(av) = 8π²(U₁₁ + U₂₂ + U₃₃)/3.

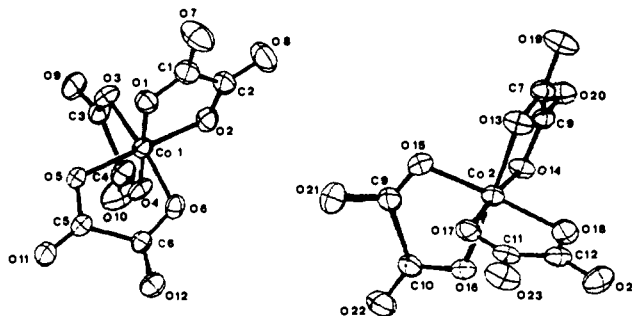


Figure 7. Numbering scheme of the complex anion in racemic-A I and optically active III crystals (left) and in racemic-B II crystals (left and right).

atoms. All cobalt atoms are octahedrally surrounded by three bidentate oxalato groups in nearly D₃ symmetry.

Table V. Final Atomic Parameters for $K_3[Co(ox)_3] \cdot 3.5H_2O$ (Racemic-B Crystal) II^a

atom	x	y	z	B(av)
Co(1)	0.17081 (4)	0.56152 (4)	0.18891 (6)	1.98
Co(2)	0.29706 (4)	0.87683 (4)	0.86727 (6)	1.83
K(1)	0.09796 (7)	0.94487 (7)	0.62064 (11)	2.80
K(2)	0.36128 (6)	0.48585 (7)	0.48475 (10)	2.33
K(3)	0.43393 (6)	0.64026 (7)	0.18964 (10)	2.27
K(4)	0.12116 (9)	0.20244 (9)	0.38496 (14)	3.90
K(5)	0.07143 (9)	0.26374 (12)	0.92359 (14)	4.23
K(6)	0.38067 (11)	0.21785 (10)	0.70264 (21)	5.33
O(1)	0.1954 (2)	0.4839 (2)	0.3645 (4)	2.90
O(2)	0.0863 (2)	0.5037 (2)	0.1384 (4)	2.77
O(3)	0.2882 (2)	0.4493 (2)	0.0469 (4)	2.57
O(4)	0.1463 (2)	0.6329 (2)	0.0077 (3)	2.27
O(5)	0.2519 (2)	0.6215 (2)	0.2512 (4)	2.37
O(6)	0.0549 (2)	0.6823 (2)	0.3189 (3)	2.23
O(7)	0.1601 (4)	0.3665 (3)	0.4640 (5)	5.83
O(8)	0.0414 (3)	0.3884 (3)	0.2214 (5)	5.10
O(9)	0.3694 (2)	0.4132 (2)	-0.2113 (4)	2.55
O(10)	0.2175 (3)	0.6129 (3)	-0.2493 (4)	3.43
O(11)	0.2284 (2)	0.7750 (2)	0.3636 (4)	3.23
O(12)	0.0169 (2)	0.8402 (2)	0.4377 (4)	2.70
O(13)	0.3791 (2)	0.7443 (2)	0.9288 (3)	2.30
O(14)	0.3310 (2)	0.8013 (2)	0.6535 (3)	1.93
O(15)	0.4135 (2)	0.8980 (2)	0.8223 (4)	2.83
O(16)	0.2213 (2)	1.0056 (2)	0.7885 (4)	2.53
O(17)	0.2622 (2)	0.9461 (2)	1.0840 (4)	2.90
O(18)	0.1766 (2)	0.8654 (2)	0.9118 (4)	2.60
O(19)	0.4728 (3)	0.5757 (2)	0.8210 (4)	3.07
O(20)	0.4244 (2)	0.6365 (2)	0.5217 (3)	2.27
O(21)	0.4539 (3)	1.0101 (3)	0.7118 (7)	5.67
O(22)	0.2486 (3)	1.1233 (3)	0.6693 (5)	4.13
O(23)	0.1380 (3)	0.9975 (3)	1.3011 (4)	3.70
O(24)	0.0431 (3)	0.9128 (3)	1.1103 (4)	3.70
C(1)	0.1519 (4)	0.4275 (3)	0.3678 (5)	3.00
C(2)	0.0855 (3)	0.4394 (3)	0.2335 (5)	2.80
C(3)	0.2998 (3)	0.4716 (3)	-0.0973 (5)	2.30
C(4)	0.2158 (3)	0.5815 (3)	-0.1201 (5)	2.40
C(5)	0.1957 (3)	0.7164 (3)	0.3251 (5)	2.17
C(6)	0.0785 (3)	0.7527 (3)	0.3645 (4)	2.13
C(7)	0.4173 (3)	0.6677 (3)	0.8111 (5)	2.07
C(8)	0.3892 (3)	0.7023 (3)	0.6458 (4)	1.80
C(9)	0.3927 (3)	0.9799 (3)	0.7555 (6)	3.07
C(10)	0.2777 (3)	1.0436 (3)	0.7337 (6)	2.67
C(11)	0.1773 (4)	0.9551 (3)	1.1601 (5)	2.37
C(12)	0.1256 (3)	0.9086 (3)	1.0566 (5)	2.33
OW(1)	0.1657 (3)	0.3791 (4)	0.8006 (5)	4.77
OW(2)	0.2503 (5)	1.1530 (5)	1.0627 (9)	7.70
OW(3)	0.3964 (5)	1.2264 (5)	1.0344 (8)	7.50
OW(4)	0.4053 (4)	0.2759 (3)	0.3979 (7)	5.57
OW(5)	0.4056 (3)	0.8444 (3)	0.3403 (6)	4.93
OW(6)	0.0164 (4)	0.8040 (4)	0.8188 (6)	6.37
OW(7)	0.3381 (8)	0.1084 (11)	0.3654 (15)	9.00
OW(7*)	0.3383 (12)	0.0880 (15)	0.2129 (22)	8.97

^aOccupancy factors for OW(7) and OW(7*) are 0.5 and 0.5, respectively. In the table of atomic parameters, standard deviations on the last significant digits are given in parentheses. Anisotropic thermal parameters are listed in Table S-5 (supplementary material). $B(av) = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

The average Co-O distances of 1.897 Å in I, 1.902 Å for Co(1) and 1.900 Å for Co(2) in II, and 1.894 Å in III are slightly shorter than the value of 1.925 Å in $K[Ni(phen)_3][Co(ox)_3] \cdot 2H_2O$.¹⁹ The O-Co-O angles in the oxalato chelates are in the range of 86.1–87.0, their average values being 86.4° in I, 86.6° and 86.4° in II, and 86.6° in III. The average C-C, inner and outer C-O distances are as follows: 1.546, 1.285, and 1.220 Å in I, 1.554, 1.285, and 1.220 Å for complex 1 in II, 1.556, 1.283, and 1.228 Å for complex 2 in II, and 1.543, 1.298, and 1.219 Å in III, respectively. Thus, there is no noticeable difference among these values. The oxygen atom coordinating directly to the Co atom is called the inner oxygen atom.

The oxalato ligands in I and II are almost planar, with maximum deviations being 0.02–0.03 Å. In III, one of the three

Table VI. Final Atomic Parameters for $\Delta\text{-}K_3[Co(ox)_3] \cdot 2H_2O$ (Optically Active Crystal) III^a

atom	x	y	z	B(av)
Co	0.51914 (11)	0.51169 (12)	0.27604 (5)	2.04
K(1)	0.41284 (24)	0.57075 (23)	0.42879 (10)	2.91
K(2)	0.57741 (27)	0.50772 (38)	0.09151 (13)	5.13
K(3)	0.92116 (24)	0.92116 (24)	0.0	2.17
K(4)	0.86690 (32)	0.86690 (32)	0.5	3.07
O(1)	0.5931 (7)	0.3956 (6)	0.2697 (3)	2.33
O(2)	0.3882 (7)	0.3797 (7)	0.3343 (3)	2.49
O(3)	0.4044 (7)	0.4213 (7)	0.2023 (3)	2.49
O(4)	0.4331 (7)	0.6198 (7)	0.2789 (3)	2.75
O(5)	0.6621 (7)	0.6454 (8)	0.2224 (3)	3.04
O(6)	0.6304 (6)	0.6066 (7)	0.3491 (3)	2.26
O(7)	0.5403 (8)	0.1826 (8)	0.2979 (4)	3.50
O(8)	0.3367 (7)	0.1805 (7)	0.3808 (3)	3.15
O(9)	0.2185 (8)	0.4053 (8)	0.1544 (4)	3.57
O(10)	0.2801 (9)	0.6480 (8)	0.2217 (3)	3.65
O(11)	0.8576 (8)	0.8429 (9)	0.2344 (3)	3.95
O(12)	0.8199 (8)	0.8059 (10)	0.3706 (3)	4.16
C(1)	0.5181 (11)	0.2781 (11)	0.3007 (4)	2.91
C(2)	0.4053 (9)	0.2753 (10)	0.3431 (4)	2.21
C(3)	0.3139 (10)	0.4593 (10)	0.1925 (4)	2.38
C(4)	0.3419 (10)	0.5858 (9)	0.2336 (4)	2.39
C(5)	0.7594 (10)	0.7412 (10)	0.2568 (4)	2.64
C(6)	0.7370 (9)	0.7211 (10)	0.3331 (3)	2.26
OW(1)	0.2366 (9)	0.1260 (9)	0.2212 (3)	3.97
OW(2)	0.3283 (11)	0.3283 (11)	0.5	3.81
OW(3)	0.3250 (18)	0.3250 (18)	0.0	7.08

^aOccupancy factors for K(3), K(4), OW(2), and OW(3) are 0.5. In the table of atomic parameters, standard deviations on the last significant digits are given in parentheses. Anisotropic thermal parameters are listed in Table S-6 (supplementary material). $B(av) = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

Table VII. Selected Bond Distances and Angles for Three Kinds of Crystals of $K_3[Co(ox)_3] \cdot nH_2O$

	rac-A I	rac-B II	act III	
Bond Distances, Å				
Co-O(1)	1.893 (3)	1.904 (4) ^a	1.897 (4) ^b	1.872 (8)
Co-O(2)	1.905 (3)	1.896 (4)	1.911 (4)	1.894 (8)
Co-O(3)	1.895 (3)	1.907 (4)	1.908 (4)	1.905 (8)
Co-O(4)	1.887 (3)	1.895 (4)	1.908 (4)	1.898 (8)
Co-O(5)	1.897 (3)	1.902 (4)	1.898 (4)	1.902 (8)
Co-O(6)	1.903 (3)	1.908 (4)	1.883 (4)	1.889 (8)
Co-K(1)	3.562 (1)		3.636 (1) ^c	3.504 (3)
Co-K(5)		3.604 (2) ^d		
Bond Angles, deg				
O(1)-Co-O(2)	86.1 (1)	86.6 (2)	86.0 (2)	86.5 (4)
O(3)-Co-O(4)	86.8 (1)	86.1 (2)	86.2 (2)	86.5 (4)
O(5)-Co-O(6)	86.3 (1)	86.4 (2)	87.0 (2)	86.7 (4)

^aAround Co(1) atom. ^bFrom Co(2) to O(13)-O(18) atoms, respectively. ^cCo(2)-K(1). ^dCo(1)-K(5). Bond distances and angles of oxalato groups are listed in Table S-7 (supplementary material).

ligands (plane 3) is also planar within 0.04 Å, but the remaining two oxalato groups (plane 1 and 2) are considerably distorted, with maximum deviations of 0.08 Å in plane 1 and of 0.15 Å in plane 2. These distortions suggest that, in crystal III, strong repulsions between the oxalato ligands of adjacent complex anions are present.

In all three crystals, one of the potassium cations K(1) approaches the Co atom directly from the threefold axis of the complex anion and comes in contact with three inner oxygen atoms of the anion, resulting in a short Co-K distance of 3.562 Å in I, 3.604 and 3.636 Å in II, and 3.504 Å in III, respectively. The same tendency had been observed previously in $rac\text{-}K_3[Rh(ox)_3] \cdot 4.5H_2O$ in which the Rh-K distance is 3.480 Å²⁰ and in optically active $\Delta\text{-}K_3[Rh(ox)_3] \cdot 2H_2O$ in which the corresponding distance is 3.494 Å.²¹

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Table VIII. Possible Interactions through Electrostatic Attraction and Hydrogen Bonding around the Potassium Ions and the Water Molecule OW(6)^a

atoms	distance, Å	mode	atoms	distance, Å	mode
(A) Racemic-A Crystal I ^b					
K(1)-O(2)	2.915 (3)	3	K(3)-O(5)	2.874 (3)	C
K(1)-O(4)	2.851 (3)	3	K(3)-O(11)	2.876 (3)	C
K(1)-O(6)	3.088 (3)	3	K(3)-O(1) ⁱⁱⁱ	2.774 (3)	C
K(1)-O(9) ⁱ	2.847 (3)	2	K(3)-O(7) ⁱⁱⁱ	2.943 (3)	C
K(1)-O(10) ⁱ	2.827 (3)	2	K(4)-O(6) ^{iv}	2.858 (3)	C
K(2)-O(3) ⁱⁱ	3.194 (3)	C	K(4)-O(12) ^{iv}	2.946 (3)	C
K(2)-O(9) ⁱⁱ	2.880 (4)	C	K(4)-O(2) ⁱⁱ	2.986 (3)	C
K(2)-O(7) ⁱⁱⁱ	2.722 (3)	2	K(4)-O(8) ⁱⁱ	2.872 (3)	C
K(2)-O(8) ⁱⁱⁱ	2.870 (4)	2			
around Co(1)			around Co(2)		
(B) Racemic-B Crystal II ^c					
K(1)-O(11)	2.858 (4)	2	K(1)-O(14)	3.162 (3)	3
K(1)-O(12)	2.838 (4)	2	K(1)-O(16)	2.864 (3)	3
K(2)-O(1)	2.804 (4)	3'	K(1)-O(18)	2.938 (3)	3
K(2)-O(5)	2.971 (3)	3'	K(2)-O(19) ⁱⁱⁱ	3.086 (3)	2
K(2)-O(9) ⁱⁱ	2.846 (4)	2	K(2)-O(20) ⁱⁱⁱ	2.823 (3)	2
K(2)-O(10) ⁱⁱ	2.728 (4)	2	K(3)-O(13) ⁱ	2.761 (4)	C
K(3)-O(5)	2.851 (3)	C	K(3)-O(19) ⁱ	3.073 (4)	C
K(3)-O(11)	2.852 (4)	C	K(6)-O(21) ^v	2.714 (6)	2
K(4)-O(7)	2.781 (6)	2	K(6)-O(22) ^v	3.928 (5)	2
K(4)-O(8)	2.944 (5)	2	OW(6)-O(18)	2.093 (6)	C
K(4)-O(6) ^{iv}	3.078 (3)	C	OW(6)-O(24)	2.994 (7)	C
K(4)-O(12) ^{iv}	2.737 (4)	C			
K(5)-O(4) ^{iv}	2.815 (4)	3'			
K(5)-O(6) ^{iv}	2.857 (4)	3'			
OW(6)-O(4) ⁱⁱ	2.851 (6)	C			
OW(6)-O(10) ⁱⁱ	2.919 (7)	C			
(C) Optically Active Crystal III ^d					
K(1)-O(2)	2.789 (8)	3	K(2)-O(7) ⁱⁱ	2.803 (10)	2
K(1)-O(4)	3.078 (9)	3	K(2)-O(8) ⁱⁱ	2.758 (9)	2
K(1)-O(6)	2.791 (8)	3	K(3)-O(11) ⁱⁱⁱ	2.992 (10)	2
K(1)-O(9) ⁱ	2.737 (9)	2	K(3)-O(12) ⁱⁱⁱ	2.735 (11)	2
K(1)-O(10) ⁱ	2.826 (10)	2			
K(2)-O(3)	2.811 (9)	3'			
K(2)-O(5)	2.982 (10)	3'			

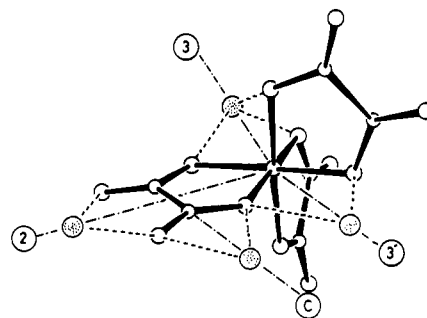
^a Selected contact mode distances are listed in this table. Full data are listed in Table S-8 (supplementary material). ^b Atoms are related to those given in Table IV as follows: i ($x, -y, 1/2 + z$); ii ($1/2 + x, 1/2 - y, 1/2 + z$); iii ($1/2 - x, -1/2 + y, 1/2 - z$); iv ($1/2 - x, 1/2 - y, 1 - z$). ^c Atoms are related to those given in Table V as follows: i ($x, y, -1 + z$); ii ($x, y, 1 + z$); iii ($1 - x, 1 - y, 1 - z$); iv ($-x, 1 - y, 1 - z$); v ($x, -1 + y, z$). ^d Atoms are related to those given in Table VI as follows: i ($1 - x, 1 + x - y, 1/3 + z$); ii ($1 + y - x, 1 - x, -1/3 + z$); iii ($1 + y - x, 2 - x, -1/3 + z$). The "mode" means "the mode of access" as shown in Figure 8.

Table IX. Least-Squares Planes and Dihedral Angles for Oxalato Groups in Optically Active Crystal^a

atom	plane 1	atom	plane 2	atom	plane 3
(a) Deviations (Å) of Atoms from Planes					
O(1)	-0.0847	O(3)	-0.1033	O(5)	0.0382
O(2)	0.0820	O(4)	0.0683	O(6)	-0.0182
O(7)	0.0675	O(9)	0.1536	O(11)	-0.0188
O(8)	-0.0736	O(10)	-0.1177	O(12)	0.0016
C(1)	0.0166	C(3)	0.0350	C(5)	-0.0142
C(2)	-0.0050	C(4)	-0.0054	C(6)	0.0160
Co	0.0693	Co	0.0398	Co	0.1817
(b) Dihedral Angles, deg					
plane 1-plane 2	92.64	plane 1-plane 3	76.36		
plane 2-plane 3	86.09				

^a Full data for I and II are listed in Table S-9 (supplementary material).

Comparison of the Crystal-Packing Modes. When a racemic complex salt crystallizes spontaneously in an optically active form, the complex ions having the same chirality should come together to form a more stable crystal structure than those of the racemic ones. Therefore, it can be expected that some chirally discrim-

**Figure 8.** Orientation of the potassium cation toward the $[\text{Co}(\text{ox})_3]^{3-}$ anion. Symbols 3, 3', 2, and C mean access 3, access 3', access 2, and access C, respectively.

inative packing modes are present in these spontaneously resolvable crystals. To search for such a characteristic feature of chiral discrimination in $\text{K}_3[\text{Co}(\text{ox})_3] \cdot n\text{H}_2\text{O}$ systems, we compared the crystal structures of I, II, and III as described below.²²

For mutual chiral discrimination between the $[\text{Co}(\text{ox})_3]^{3-}$ anions, they must come close to each other. The potassium cations must be present between these $[\text{Co}(\text{ox})_3]^{3-}$ anions in order to reduce the electrostatic repulsion. We identified those potassium cations which are strongly attracted to two or more complex anions and classified them into the following four groups as shown in Figure 8: (1) The orientation labeled 3 in Figure 8 is called access 3. In this position, the K^+ ion is linked with inner oxygen atoms of three different oxalato ligands in a complex anion. (2) The orientation labeled 2 is called access 2, in which the K^+ ion is linked to two outer oxygen atoms of the same oxalato ligand. (3) The orientation labeled C is called access C, in which the K^+ ion is linked to one inner and one outer oxygen atom of the same oxalato chelate ring.

The schematic representations of three crystal structures I, II, and III illustrating above mentioned contact modes are shown in Figure 9. We can classify the potassium cations into the following three groups: (1) The K^+ ion labeled as K(1), which has both access 3 and access 2 toward the adjacent complex anions, is found in all crystals. K(1) in II and in III connects two complex anions having the same chirality, while K(1) in I connects with four adjacent complex anions, two of each chirality. (2) The K^+ ion labeled as K(2), which has access 3' and access 2 between two complex anions, is found in II and III. The complex anions connected by K(2) have the same chirality both in II and III. Such a K^+ ion does not exist in I. (3) The K^+ ion labeled as K(3), which has access C to two complex anions having the same chirality, is found in I. Such a K^+ ion does not exist in II and III, but in II the water molecule OW(6) is found to play the same role as K(3) in I.

From the above discussion, it is seen that, although two racemic crystal forms were obtained, the crystal packing mode of II bears a close resemblance to that found in III. This result is consistent with the fact that the thermal behavior of III resembles that of II more than that of I.²³

Origin of Chiral Discrimination. Now, we can compare the crystal structure of II with that of III in more detail. In II, two types of potassium cations (K(1) and K(2)), one water molecule

(22) Though the numbers of water of crystallization are different in the present $\text{K}_3[\text{Co}(\text{ox})_3]$ series, the following results, (1), (2), and (2)', suggest that the difference in the lattice energy among them is probably very small. (1) Three polymorphic crystals I, II, and III are deposited simultaneously at the temperature range 10–20 °C as shown in Table I. (2) The densities for three crystals (2.12 for I, 2.10 for II, and 2.13 g/cm³ for III as shown in Table III) are nearly equal. (2)' The effective volumes of $\text{K}_3[\text{Co}(\text{ox})_3]$ unit, V^* in Table III, 332 for I, 326 for II, and 330 Å³ for III are nearly equal.

(23) I and III are equal (dihydrate), but II is different (3.5 hydrate) in the number of waters of crystallization. But our results suggest that II and III have some common features in their thermal behaviors and crystal structures.

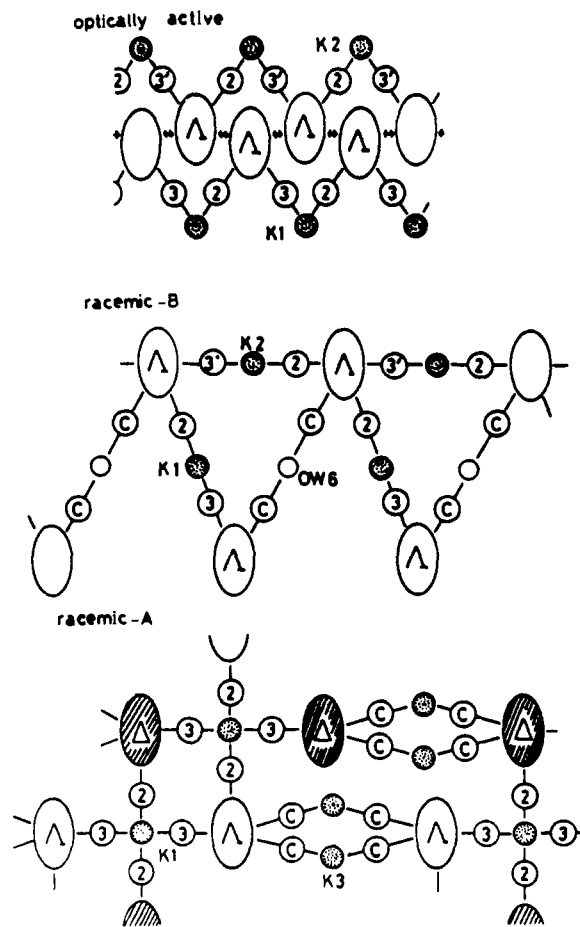


Figure 9. Schematic representation of three kinds of crystal structures spotlighted on the direct contact mode between potassium cation and complex anion.

(OW(6)), and two crystallographically independent complex anions (Co(1) and Co(2)) having the same chirality are arranged in a zigzag manner along the c axis to form a chiral, columnar structure. An enantiomeric column is generated by the crystallographic inversion centers. Figure 10 shows a schematic representation of this arrangement, in which the columns contact each other in a side-by-side fashion. Among these columns, the remaining K^+ ions and water molecules complete the three-dimensional structures. The complex anions are strongly held together in the direction of the axes of the individual columns. In contrast, between the columns the interactions mainly come from the close contacts through the water molecules (see Table S-8), and chiral discriminative power between the columns in II is weak.

The corresponding arrangement in III is illustrated in Figure 11.²⁴ Two kinds of spiral $-K$ -complex- K -complex- sequences are found; one is composed of K(1) and complex anions which have three oxalato chelate rings numbered 1, 3, and 5, and the other is composed of K(2) and complex anions having rings

(24) The steps to make Figure 11 are illustrated in detail in the supplementary materials with six figures (Figures 12-17). The steps are as follows. (1) There are three crystallographically independent oxalato groups, plane 1, plane 2, and plane 3, as shown in Table IX. From the operation of 3_1 screw axis, nine planes are generated around it and stacked along the c axis. However, the plane 3 is quite parallel to the c axis, and they cannot stack efficiently along the c axis. Thus, six chelate rings which are numbered 1, 3, 5 and 2, 4, 6 remained. (2) The relation among the plane 1 and plane 2 and the ring 1 to 6 is then clear: if ring 1 is plane 1, then ring 2 is plane 2. Rings 3 and 5 are generated from plane 1, and rings 4 and 6 are generated from plane 2. (3) The potassium cation K(1) is linked to ring 1 by the mode of access 2, and the same K(1) is linked to the complex anion by access 3 as shown in Figure 9. This complex has ring 3, and it plays a role of ring 1 in the preceding step, and so on. The relations from K(2) to the rings 2, 4, and 6 are quite similar to those around the K(1). Thus, two kinds of spiral $-K$ -complex- K -complex- sequences around the 3_1 screw axis are formed in the double helical fashion.

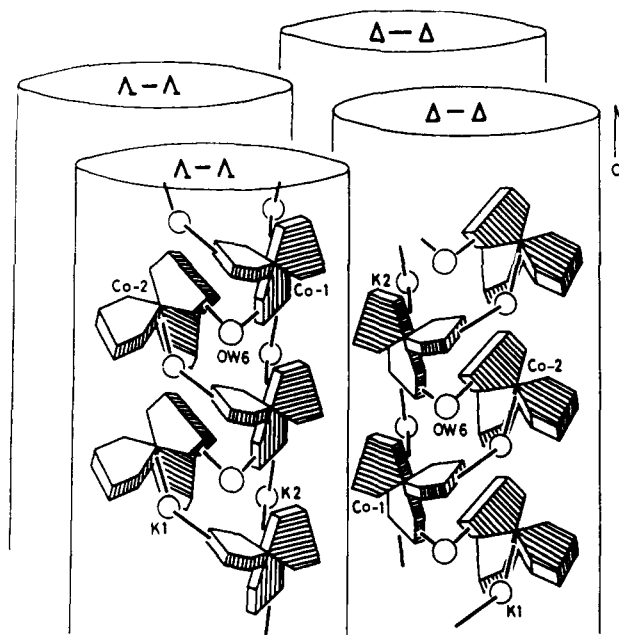


Figure 10. Schematic representation of the arrangement composed of $[Co(ox)_3]^{3-}$, K(1), K(2), and OW(6), in racemic-B crystal II.

numbered 2, 4, and 6. These two spiral chains combine along the c axis to form a right-handed double helix structure, and the helix fills a triangular prism unit in this crystal (space group $P3_121$ for the Λ complex) as shown in Figure 11. Several short contacts between the adjacent oxalato-oxalato planes which belong to the different spiral chains in the double helix are found. As mentioned previously, these chelate rings deviate considerably from a plane (plane 1 and plane 2), probably due to mutual repulsion. In other words, the chiral discrimination does not take place between the complex anions in the same spiral chain but between the complex anions in different spiral chains within a double helix. Around this chiral double helix, the remaining K^+ cations and water molecules complete the three-dimensional structure.

In III, it is interesting to note that only one crystallographically independent complex anion having three oxalato groups is present, but this complex anion forms two different spiral chains with the two crystallographically independent potassium cations. In Figure 11, each of the oxalato chelates in the complexes within a triangular prism fulfills the requirement of one-dimensional chiral discrimination along the c axis. At the same time, the close contacts about the outer oxygen atoms of the remaining oxalato rings fulfill the requirement of two-dimensional discrimination toward the adjacent double helix. The result is three-dimensional discrimination.

Comparison with Other Metal(III) Structures. Recently, Kuroda and Mason compared the crystal structures of optically active and racemic $[Cr(pd)_3]$, $pd = \text{pentane-2,4-dionato}$, in which the complex molecule has a D_3 symmetry.²⁵ They found that both crystals have a characteristic columnar arrangement of complexes in which the chelate rings of contiguous complexes are disposed parallel to each other. These columns pack more compactly in the plane which is orthogonal with those parallel axes, when adjacent columns contain racemic pairs. Therefore, in the neutral complex, the packing mode is mainly controlled by the requirement of compact fitting of the component molecules.

In contrast, in the present $K_3[Co(ox)_3] \cdot nH_2O$ series (the complex anion still has a D_3 symmetry), the electrostatic interaction is the dominant factor. The known crystal structures of $K_3[M(ox)_3] \cdot nH_2O$ where $M = Al, V, Cr, Mn, Fe, Co, Rh,$ and Ir are summarized in Table X with the number of the respective "mode of access" between the complex anion and the potassium cation.²⁶⁻²⁹ There are six types of crystal structures: I, II, V, and

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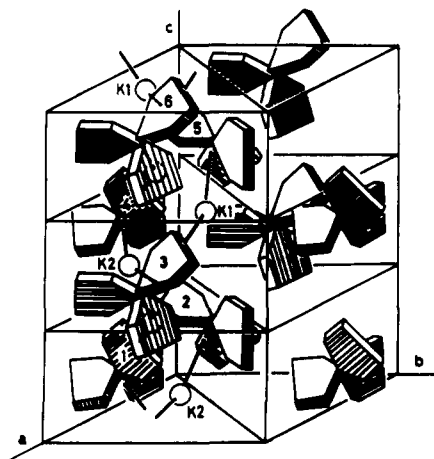


Figure 11. Schematic representation of the arrangement composed of $[\text{Co}(\text{ox})_3]^{3-}$, K(1), and K(2), in optically active crystal III.

Table X. Known Types of Crystal Structures of Racemic and Optically Active $\text{K}_3[\text{M}(\text{ox})_3] \cdot n\text{H}_2\text{O}$ and the Numbers of "Mode of Access" between the $[\text{M}(\text{ox})_3]^{3-}$ and the Potassium Cation^a

type	M	space group	Z	n	mode of access				ref	
					3	3'	C	2		
I	Co(rac-A)	$C2/c$	8	2	1	0	5	2	b	
II	Co(rac-B)	$P\bar{1}$	4	3.5	Co(1)	0	2	3	3	c
					Co(2)	1	0	2	2	
III	Co, Rh	$P3_121$	6	2	1	1	0	3	d	
IV	Ir	$P3_221$	3	2	0	2	0	0	e	
V	Al, V, Cr	$P2_1/c$	4	3	0	0	0	2	f	
VI	Rh, Ir	$P\bar{1}$	2	4.5	1	0	2	2	g	

^a The K-O contact distances in this table are less than 3.0 Å. ^b This work (Co-K 3.562 Å). ^c This work (Co(1)-K 3.604 and 3.841 Å and Co(2)-K 3.636 Å). ^d Co, this work (Co-K 3.504 and 3.806 Å) and Rh (ref 21) (Rh-K 3.494 and 3.827 Å). ^e Reference 7; Ir is not isomorphous with Co and Rh (Ir-K 3.65 Å). ^f Al, ref 26; V, ref 27; Cr, ref 26; Mn, ref 28; and Fe, ref 29. ^g Rh, ref 20 (Rh-K 3.480 Å) and Ir (ref 7). Crystal types I, II, V, and VI are racemic forms and III and IV are optically active forms, respectively.

VI are racemic ones and III and IV are optically active.

It is interesting to note that (1) access 3 and 3' are found only in the Co, Rh, and Ir complexes (low-spin d^6 electronic configuration), and for the racemic crystals VI, Rh and Ir are in isomorphous, while for the optically active ones III Co and Rh are in isomorphous.³⁰ (2) The remaining racemic Al, V, Cr, Mn,

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and Fe complexes are all isomorphous.³¹ (3) The heterochiral columnar structure (Δ complex-K⁺- Δ complex-K⁺) in which the chelate rings of contiguous complexes are disposed nearly parallel is found in I, V, and VI. (4) No contact between the Δ complex and the Λ complex is found in I, V, and VI. (5) The homochiral zigzag chain as shown in Figure 10, in which the dihedral angle of contiguous chelate rings is about 43°, is found in II. (6) A double spiral type homochiral columnar structure, in which the contiguous chelate rings (rings; 1-2, 3-4, and 5-6 in Figure 11) are disposed almost perpendicular (averaged dihedral angle is 81° (Co) and 82° (Rh)), is found in III.³²

Therefore, in the $\text{K}_3[\text{M}(\text{ox})_3] \cdot n\text{H}_2\text{O}$ crystals, "a parallel superposition of contiguous chelate rings for the neutral D_3 complex" proposed by Kuroda and Mason occurs in the racemic crystals of I, V, and VI but does not occur in crystals II and III, which are involved in the spontaneous resolution. Thus, in the spontaneous resolution of $\text{K}_3[\text{Co}(\text{ox})_3] \cdot n\text{H}_2\text{O}$, the crystal-packing modes reported here which discriminate between the charged enantiomeric tris-chelate metal complexes represent a new type of effect.

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Registry No. I, 96413-15-9; II, 27736-00-1; III, 96413-16-0.

Supplementary Material Available: Observed and calculated structure factors from the respective final cycles of least-squares refinement (Tables S-1, 2, and 3), listings of anisotropic thermal parameters for non-hydrogen atoms (Tables S-4, 5, and 6), bond lengths and angles (Tables S-7 and 8), least-squares planes (Table S-9), and Figures 2, 4, 5, 6, and 12-17 (35 pages). Ordering information is given on any current masthead page.

(30) The first claim for spontaneous resolution of a metal complex was made by Werner for $\text{K}_3[\text{Rh}(\text{ox})_3] \cdot \text{H}_2\text{O}$ in 1914 (Werner, A. *Ber.* **1914**, *47*, 1954). He gave a sketch of spontaneously resolved pairs of crystals, but our reexamination showed that his sketch was quite the same as with the shape of racemic ones which we obtained. Jaeger (ref 4) and Gillard et al. (ref 5) also reported that they were unable to repeat Werner's claim for spontaneous resolution of racemic $\text{K}_3[\text{Rh}(\text{ox})_3] \cdot 4.5\text{H}_2\text{O}$. However, the optically active form of $\text{K}_3[\text{Rh}(\text{ox})_3] \cdot 2\text{H}_2\text{O}$ is isomorphous with the spontaneously resolvable Co analogue. The difference between the Rh and Co is only in their racemic state. We have to examine the spontaneous resolution for the Rh one more carefully (solubility isotherm study is planned).

(31) The reported IR data for the symmetric and asymmetric carbonyl stretching modes, $\nu_s(\text{C}=\text{O})$ and $\nu_{as}(\text{C}=\text{O})$, respectively, in the $\text{K}_3[\text{M}(\text{ox})_3] \cdot n\text{H}_2\text{O}$ series are shown that the C=O double bonds in the complex anions with a low-spin d^6 electronic configuration are more ionic than those in other complex anions (M = V, Cr, Mn, and Fe). Gouteron, J. *J. Inorg. Nucl. Chem.* **1976**, *38* (1), 55.

(32) The crystal packing of optically active $\text{K}_3[\text{Ir}(\text{ox})_3] \cdot 2\text{H}_2\text{O}$, IV, is quite different from those of Co and Rh. Apparently, the space groups of them are equal, but the cell length of c axis in Ir complex is 10.38 Å and Z = 3 (20.291 Å for Co and 20.339 Å for Rh ones and Z = 6). The crystallographic twofold axis through the complex anion exactly at the Ir position and 1.5 oxalato groups are crystallographically independent. Thus, only a single helical structure can be made around the 3_2 screw axis.