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The Crystal Structure of the Spontaneously Resolved Λ(R,R)Δ(G,R)-Aquo(ethylenediaminetriacetatoacetic acid)cobalt(III) Trihydrate, Λ(R,R)Δ(G,R)-[Co(Hedta)H_2O]$\cdot 3H_2O$*

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Aquo(ethylenediaminetriacetatoacetic acid)cobalt(III) [Co(Hedta)H_2O], prepared from an acidic solution (pH < 1) of K[Co(edta)], has been found to be resolved spontaneously and its crystal structure has been determined by single crystal X-ray diffraction techniques. Crystal data are as follows: Λ(R,R)-Δ(G,R)-[Co($C_{10}H_{13}N_2O_8$)H_2O]$\cdot 3H_2O$, orthorhombic, space group $P2_12_12_1$, *a = 25.880(2)* Å, *b = 14.699(1)* Å, *c = 8.453(1)* Å, *Z = 8, R = 0.054. The spontaneously resolved [Co(Hedta)H_2O]$\cdot 3H_2O$ is different in crystal structure from the corresponding complexes of the other metal ions [M(Hedta)H_2O] (M = Rh, Fe, Cr, and Ga) crystallized similarly, which are all racemic and isomorphous. The crystal lattice is composed of two crystallographically independent complexes and water molecules. The uncoordinated protonated acetate group (–CH_2COOH) has the same conformation in the two independent complexes. This conformation is also found in other [M(Hedta)-H_2O] complexes. Each uncoordinated –CH_2COOH arm is involved in hydrogen bonding with one molecule of water of crystallization. The complexes are linked with one another through the intermolecular hydrogen bonding between the coordinated water molecule and the uncoordinated oxygen atom, forming right-handed pseudo-4_1 spiral chains along the twofold screw axes parallel to the a axis. By comparison of these homochiral spiral chains with the corresponding 2_1 chains found in the other metal complexes, [M(Hedta)H_2O], formed by the hydrogen bonding similar to the pseudo-4_1 chains in [Co-(Hedta)H_2O]$\cdot 3H_2O$, the characteristic packing mode in the title compound can be evaluated.*

Introduction

Only a few examples of spontaneously resolved complex compounds have been reported to date. These include $K_3[Co(ox)_3]\cdot 2H_2O$ [1], Y[M(edta)]$\cdot$ $2H_2O$ (Y = K, NH_4, and Rb; M = Al, Cr, and Co) [2–5], $[Co(NO_2)_2(en)_2]X$ (X = Cl, Br, and NO_2) [5, 6], and $[Co(ox)(en)_2]X$ (X = Cl$\cdot 4H_2O$ and Br$\cdot$ H_2O [5, 7] *etc.* [8].

Since the solvation energy is the same for both types of enantiomers, the solubilities of the racemic and optically active crystals are dependent solely on the magnitudes of their lattice energies. If their lattice energies are quite close to each other, then the solubility of the racemic crystals should be quite close to that of the active crystals. Since the saturated solution of the racemic crystals contains equal amounts of two kinds of enantiomers, the concentration of one type of enantiomers, say the d form, is only one half of the concentration of the same enantiomer in the saturated solution of the active crystals. Thus the saturated solution of the racemic crystals does not satisfy the conditions for the active crystals to come out. For the active crystals to come out, the solubility of the active crystals should be much less than that of the corresponding imaginary racemic crystals. Therefore, it is expected that spontaneous resolution occurs when the active crystals have a unique packing mode and a large lattice energy which any imaginary racemic crystals cannot exceed.

Such a unique packing mode has been found recently in the case of $K_3[Co(ox)_3]\cdot nH_2O$ [9]. As this is an ionic crystal, the packing mode of the chiral complex ions is affected by the counter ions. Substitution of Na^+ for K^+, for example, destroys such a unique structure. In the case of an uncharged chiral molecule, the crystal packing mode depends primarily on the character of the chiral molecule itself. Thus when it is spontaneously resolved, a unique packing

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*The absolute configuration 'Λ(R,R)Δ(G,R)' represents that two R rings (R1 and R2) take Λ configuration and that one R ring (R2) and G ring take Δ configuration.

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mode, which enables the three-dimensional chiral discrimination, should be found in a simple way. It is well-known that Y[Co(edta)]$\cdot$nH_2O (Y = K^+, NH_4^+) can be spontaneously resolved [5]. Recently, it has been found that aquo(ethylenediaminetriacetatoacetic acid)cobalt(III), [Co(Hedta)H_2O], prepared from the acidic solution (pH < 1) of K[Co(edta)] is spontaneously resolved. On the other hand, it has already been reported [10, 11] that the corresponding [M(Hedta)H_2O] of other metals (M = Rh, Fe, Cr, and Ga) are all racemic and isomorphous. The present study was undertaken to determine the crystal structure of the spontaneously resolved [Co(Hedta)H_2O] and to find out the nature of the chiral discrimiation in the crystal.

Experimental

K[Co(edta)]$\cdot$2H_2O, prepared according to the literature [12], was passed through a column of the H^+-form of Dowex 50W. Red-violet needle crystals were obtained by slow evaporation of the effluent solution, with the deposition of crystals occuring at pH = *ca.* 0.4 (*Anal.* Found: C, 28.6; H, 5.0; N, 6.6%. Calcd. for $C_{10}H_{21}CoN_2O_{12}$: C, 28.58; H, 5.03; N, 6.67%). Circular dichroism (CD) spectra were measured on a JASCO J-40CS recording spectropolarimeter to confirm the spontaneous resolution of obtained crystals.

The crystal used for the data collection had dimensions of 0.51 × 0.44 × 0.35 mm. The determination of cell constants and the intensity data collection were carried out on a Rigaku AFC-5 automated four circle diffractometer with Mo-Kα radiation (λ = 0.71069 Å) monochromated by a graphite plate. The cell constants, determined by a least-squares method using 25 independent reflections ($2\theta > 28°$), were a = 25.880(2) Å, b = 14.669(1) Å, c = 8.453(1) Å, and V = 3215.5(6) Å^3. The space group was determined as $P2_12_12_1$ (D_2^4, No. 19) from the systematic absences for h00 (h = 2n + 1), 0k0 (k = 2n + 1), and 00l (l = 2n + 1). The measured density of 1.73 g cm^{-3} obtained by the flotation technique using a $CHCl_3$–$CHBr_3$ mixed solution agrees well with the calculated value of 1.74 g cm^{-3} for Z = 8. The intensity data were collected by the ω–2θ scan technique to a maximum 2θ value of 55° over the scan rate range of 8° min^{-1} (50 kV, 170 mA). The ω scan range was $(1.2 + 0.5 \tan\theta)°$. As a check on experimental stability, intensities of three standard reflections were monitored at intervals of 200 reflections. Out of 4226 independent reflections measured, 3534 reflections of $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. No absorption correction was made since the linear absorption coefficient of μ(Mo-Kα) = 11.8 cm^{-1} was low.

The structure was solved by standard heavy-atom techniques and refined by block-diagonal least-squares methods. The positions of two Co atoms (Co(A) and Co(B)) were determined from the three-dimensional Patterson map. Subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. After all the non-hydrogen atoms were refined isotropically, a series of refinements using anisotropic thermal parameters for non-hydrogen atoms reduced an R value, $\Sigma||Fo| - |Fc||/\Sigma|Fo|$, to 0.076 and an R_w value, $[\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$, to 0.076. All the hydrogen atoms were located from subsequent difference Fourier maps. All atoms were further refined, non-hydrogen atoms anisotropically and hydrogen atoms isotropically. A final refinement converged R to 0.054 and R_w to 0.070. A final difference Fourier map revealed no peaks higher than 0.3 e Å^{-3}. The quantity minimized was $\Sigma w(|Fo| - k|Fc|)^2$. The weighting scheme used was $w = (\sigma_{cs} + a|Fo|^2 + b|Fo|)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics for each reflection and values of a and b used in the final refinement are 0.0009 and 0.2 respectively. Absolute configuration of the complex was determined by using the anomalous dispersion coefficients of Cromer and Liberman [13]. All the atomic scattering factors were taken from Cromer and Waber [14]. The final atomic coordinates and final thermal parameters are given in Table I, according to the atom labels of Figs. 1a and 1b. All the computations were carried out by a HITAC M-200H computer at the Hiroshima University Information Processing Center. The computer programs used were Four-MMM (Fourier syntheses) [15], and HBLS-IV (least-squares calculation) with a slight modification [16]. ORTEP drawing [17]

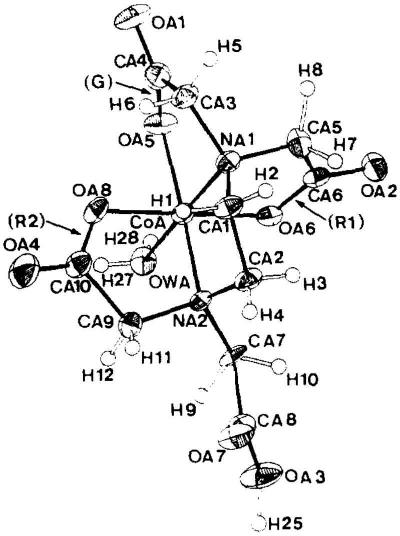

Fig. 1a. A perspective view of Λ(R,R)Δ(G,R)-'complex-A' with the atom numbering scheme.

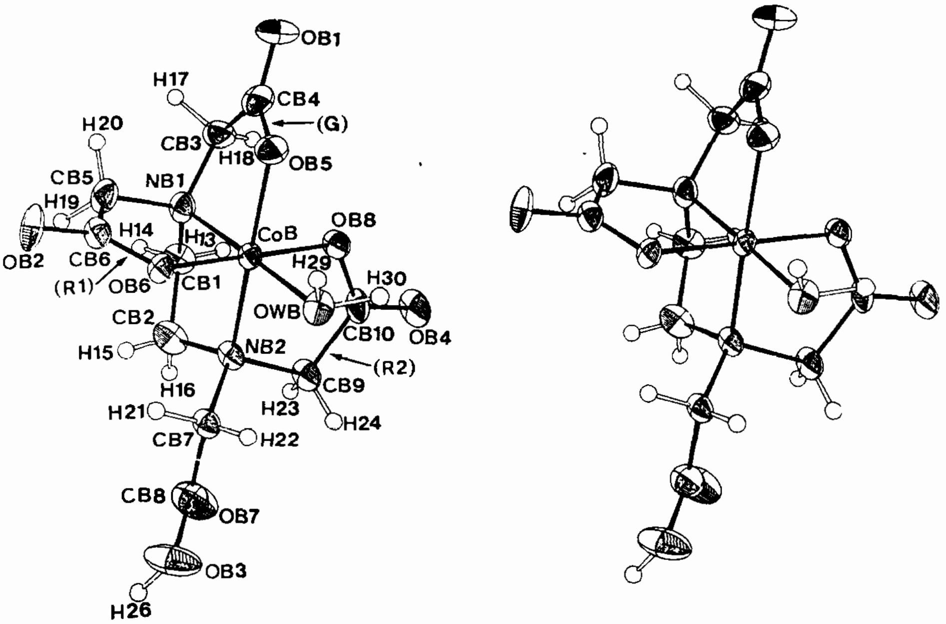

Fig. 1b. A stereoview of Λ(R,R)Δ(G,R)-'complex-B' with the atom numbering scheme.

TABLE I. Atomic Coordinates and Thermal Parameters for $[Co(Hedta)H_2O] \cdot 3H_2O$.[a]

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
CO(A)	4460(0)	1876(1)	3150(1)	222(4)	244(4)	120(3)	0(3)	–4(3)	11(3)
OA(1)	4634(2)	3242(4)	7031(6)	558(36)	426(29)	229(24)	102(27)	–36(24)	–141(24)
OA(2)	5798(2)	2707(4)	1616(5)	254(25)	557(31)	161(21)	–70(23)	–20(19)	80(24)
OA(3)	4313(3)	32(4)	–2113(6)	792(48)	460(31)	126(22)	–115(32)	–55(25)	–8(22)
OA(4)	3426(3)	232(4)	4909(7)	512(39)	509(34)	372(31)	–154(30)	204(28)	–16(28)
OA(5)	4485(2)	2919(3)	4500(6)	403(28)	246(22)	216(21)	10(21)	–82(22)	–32(19)
OA(6)	4962(2)	2372(3)	1763(6)	280(23)	297(22)	179(20)	–28(19)	–9(20)	60(21)
OA(7)	4416(3)	–872(3)	–9(6)	582(40)	317(26)	267(26)	–31(26)	5(26)	–54(21)
OA(8)	3958(2)	1399(3)	4530(5)	305(26)	328(24)	154(20)	5(21)	82(20)	8(20)
NA(1)	5021(2)	1432(4)	4453(6)	271(29)	234(24)	112(21)	12(22)	1(21)	25(21)
NA(2)	4436(2)	679(4)	2061(5)	230(27)	315(26)	65(70)	–51(22)	28(19)	1(20)
CA(1)	5008(3)	415(4)	4362(8)	409(41)	226(29)	143(27)	8(29)	7(27)	17(25)
CA(2)	4907(3)	182(5)	2623(8)	287(40)	379(36)	137(27)	87(30)	–49(26)	–40(27)
CA(3)	4913(3)	1800(5)	6061(7)	343(39)	318(33)	146(27)	–16(30)	12(26)	–17(27)
CA(4)	4666(3)	2726(5)	5868(8)	251(34)	324(33)	247(31)	31(29)	0(26)	10(30)
CA(5)	5505(3)	1835(5)	3810(8)	209(32)	405(35)	193(28)	–8(31)	–39(25)	104(29)
CA(6)	5421(3)	2348(4)	2291(7)	305(35)	232(29)	124(25)	6(26)	–15(23)	–20(23)
CA(7)	4444(3)	776(4)	308(7)	374(38)	277(30)	55(23)	4(29)	47(25)	–22(22)
CA(8)	4390(3)	–137(5)	–559(8)	302(40)	365(35)	152(28)	–57(29)	–8(26)	3(27)
CA(9)	3946(3)	228(5)	2586(8)	262(36)	358(36)	198(29)	–97(29)	48(27)	28(28)
CA(10)	3756(3)	626(5)	4155(8)	324(38)	295(32)	204(30)	–36(29)	50(27)	36(27)
CO(B)	2260(0)	2751(1)	6784(1)	230(4)	251(4)	109(3)	36(3)	13(3)	8(4)
OB(1)	2051(3)	5272(4)	5612(8)	632(43)	333(28)	578(39)	137(29)	27(36)	210(30)
OB(2)	3011(2)	2347(4)	2881(5)	289(27)	614(34)	155(21)	–32(25)	83(19)	–79(23)
OB(3)	2735(3)	–638(4)	7837(7)	1071(60)	264(25)	313(29)	151(34)	–224(35)	–7(24)
OB(4)	1879(2)	2975(4)	11205(6)	574(37)	507(33)	156(21)	199(29)	141(23)	–23(23)
OB(5)	1965(2)	3770(3)	5714(6)	395(31)	336(25)	233(23)	97(23)	33(22)	66(21)
OB(6)	2463(2)	2217(3)	4880(5)	293(25)	299(22)	101(18)	29(20)	16(17)	–4(19)
OB(7)	3100(3)	298(4)	9610(7)	685(46)	423(30)	339(30)	175(31)	–204(30)	–8(27)

(continued overleaf)

TABLE I. *(continued)*

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
OB(8)	2031(2)	3284(3)	8680(5)	393(28)	308(24)	152(20)	128(22)	66(20)	14(19)
NB(1)	2886(2)	3454(4)	6714(7)	302(30)	274(25)	223(25)	−13(22)	37(25)	−66(25)
NB(2)	2612(2)	1828(4)	8107(6)	287(28)	246(24)	131(22)	65(21)	−31(21)	−51(24)
CB(1)	3205(3)	3141(5)	8093(9)	266(33)	322(31)	296(33)	0(28)	−103(31)	−51(34)
CB(2)	3167(3)	2110(5)	8141(10)	288(34)	354(35)	378(37)	64(29)	−133(34)	−39(36)
CB(3)	2724(3)	4430(5)	6853(10)	489(44)	235(29)	310(35)	34(31)	48(40)	−18(32)
CB(4)	2207(3)	4524(5)	5976(8)	494(49)	361(37)	189(31)	43(36)	60(31)	49(29)
CB(5)	3144(3)	3287(5)	5156(8)	409(43)	363(38)	218(31)	−47(33)	116(30)	−60(30)
CB(6)	2861(3)	2559(5)	4232(7)	269(36)	310(32)	137(26)	61(26)	1(24)	−8(24)
CB(7)	2565(3)	891(4)	7480(8)	282(35)	235(30)	171(27)	43(26)	3(26)	−34(25)
CB(8)	2834(3)	164(5)	8417(9)	507(51)	322(35)	262(36)	91(34)	−3(34)	−16(30)
CB(9)	2350(3)	1872(5)	9723(7)	410(43)	360(34)	129(26)	127(33)	43(27)	−11(28)
CB(10)	2068(3)	2764(5)	9930(8)	284(35)	423(38)	180(28)	88(31)	86(27)	−21(30)
OW(A)	3938(2)	2397(3)	1793(6)	251(23)	331(23)	214(21)	25(19)	−11(21)	92(22)
OW(B)	1642(2)	2019(3)	6670(6)	222(23)	393(26)	212(21)	4(19)	−31(20)	34(21)
OW(1)	557(4)	4923(5)	1316(10)	766(56)	688(45)	646(47)	242(43)	−143(43)	3(40)
OW(2)	573(3)	1538(4)	1381(6)	512(37)	575(34)	270(26)	0(30)	66(26)	158(26)
OW(3)	1044(3)	5804(4)	6322(9)	511(40)	463(34)	612(42)	−26(30)	17(34)	−70(32)
OW(4)	1239(3)	4069(5)	3204(9)	769(52)	769(46)	419(34)	275(40)	−159(40)	−58(39)
OW(5)	1226(4)	4685(5)	8815(10)	912(64)	612(43)	659(47)	346(44)	178(46)	127(40)
OW(6)	1449(3)	1909(4)	3568(7)	511(36)	493(31)	331(29)	−133(30)	−76(26)	25(26)

Atom	X	Y	Z	B, Å	Atom	X	Y	Z	B, Å
H(1)	473(4)	16(6)	495(12)	2.13(225)	H(22)	223(4)	73(7)	753(12)	2.30(229)
H(2)	536(4)	17(6)	467(13)	2.25(228)	H(23)	263(4)	182(7)	1045(13)	2.53(331)
H(3)	520(4)	38(7)	210(13)	2.35(231)	H(24)	212(4)	132(7)	990(12)	2.21(227)
H(4)	490(4)	−50(6)	251(12)	1.40(196)	H(25)	421(5)	−57(8)	−264(14)	3.44(276)
H(5)	521(4)	187(7)	665(12)	2.13(209)	H(26)	304(4)	−100(8)	809(14)	3.27(257)
H(6)	468(4)	137(6)	662(12)	1.98(212)	H(27)	364(4)	239(7)	212(12)	2.09(214)
H(7)	576(4)	131(7)	357(14)	3.53(274)	H(28)	399(5)	284(8)	177(14)	3.85(280)
H(8)	570(4)	227(7)	462(13)	2.46(228)	H(29)	149(4)	216(7)	586(13)	2.82(250)
H(9)	411(6)	59(10)	−17(17)	6.16(383)	H(30)	136(5)	227(8)	738(14)	3.93(295)
H(10)	474(6)	58(10)	−19(18)	6.77(424)	H(31)	75(5)	545(8)	116(14)	3.86(293)
H(11)	398(4)	−45(6)	271(11)	1.22(191)	H(32)	85(5)	457(8)	218(14)	3.82(289)
H(12)	366(4)	34(7)	187(13)	2.49(225)	H(33)	29(4)	177(8)	158(14)	3.50(271)
H(13)	306(5)	343(7)	899(13)	2.98(257)	H(34)	67(5)	195(8)	25(16)	5.06(342)
H(14)	358(5)	335(8)	808(15)	3.80(279)	H(35)	115(5)	548(8)	738(13)	3.13(265)
H(15)	334(4)	182(7)	741(13)	2.73(244)	H(36)	136(4)	580(7)	580(13)	2.79(248)
H(16)	338(4)	186(7)	909(13)	2.51(230)	H(37)	147(5)	427(8)	398(14)	3.71(284)
H(17)	300(4)	484(7)	623(12)	2.50(239)	H(38)	142(5)	364(9)	221(16)	4.96(344)
H(18)	269(4)	462(7)	787(13)	2.60(239)	H(39)	140(4)	405(8)	877(14)	3.46(281)
H(19)	354(4)	307(7)	533(14)	3.38(267)	H(40)	102(5)	466(8)	979(15)	4.15(305)
H(20)	317(5)	389(9)	470(16)	4.89(333)	H(41)	108(5)	177(8)	292(15)	4.24(301)
H(21)	273(4)	88(7)	648(13)	2.78(246)	H(42)	159(4)	245(8)	304(14)	3.75(273)

[a] All quantities except for isotropic thermal parameters are $\times 10^4$. The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

was carried out by the computer system XTL in a Syntex R3 automated four-circle diffractometer. A table of observed and calculated structure factor amplitudes is available upon request to the author (H.Y.).

Results and Discussion

Confirmation of Spontaneous Resolution

The CD spectrum of the solution prepared by dissolving a grain of single crystal in water gives

TABLE II. Intramolecular Bond Distances (Å) with Least-Squares Estimated Standard Deviations in Parentheses.

Atoms	Distances (Å)	Atoms	Distances (Å)
Co(A)–NA(1)	1.937(6)	Co(B)–NB(1)	1.925(6)
Co(A)–NA(2)	1.986(6)	Co(B)–NB(2)	1.978(5)
Co(A)–OA(5)	1.913(6)	Co(B)–OB(5)	1.908(6)
Co(A)–OA(6)	1.896(5)	Co(B)–OB(6)	1.865(5)
Co(A)–OA(8)	1.881(5)	Co(B)–OB(8)	1.879(6)
Co(A)–OW(A)	1.927(5)	Co(B)–OW(B)	1.929(5)
NA(1)–CA(1)	1.498(10)	NB(1)–CB(1)	1.499(9)
NA(1)–CA(3)	1.490(9)	NB(1)–CB(3)	1.499(10)
NA(1)–CA(5)	1.486(9)	NB(1)–CB(5)	1.497(10)
NA(2)–CA(2)	1.497(9)	NB(2)–CB(2)	1.500(10)
NA(2)–CA(7)	1.489(9)	NB(2)–CB(7)	1.481(9)
NA(2)–CA(9)	1.498(9)	NB(2)–CB(9)	1.526(10)
CA(1)–CA(2)	1.532(11)	CB(1)–CB(2)	1.511(11)
CA(3)–CA(4)	1.514(10)	CB(3)–CB(4)	1.535(12)
CA(5)–CA(6)	1.503(10)	DB(5)–CB(6)	1.512(11)
CA(7)–CA(8)	1.528(11)	CB(7)–CB(8)	1.499(11)
CA(9)–CA(10)	1.530(11)	CB(9)–CB(10)	1.506(11)
OA(5)–CA(4)	1.278(9)	OB(5)–CB(4)	1.293(10)
OA(6)–CA(6)	1.271(8)	OB(6)–CB(6)	1.271(8)
OA(8)–CA(10)	1.293(9)	OB(8)–CB(10)	1.307(10)
OA(1)–CA(4)	1.242(10)	OB(1)–CB(4)	1.213(11)
OA(2)–CA(6)	1.247(9)	OB(2)–CB(6)	1.246(9)
OA(4)–CA(10)	1.213(10)	OB(4)–CB(10)	1.222(10)
OA(3)–CA(8)	1.352(10)	OB(3)–CB(8)	1.297(12)
OA(7)–CA(8)	1.180(10)	OB(7)–CB(8)	1.238(11)

TABLE III. Intramolecular Bond Angles (°) with Least-Squares Estimated Standard Deviations in Parentheses.

Atoms	Angles (°)	Atoms	Angles (°)
NA(1)–Co(A)–OA(5)	84.5(2)	NB(1)–Co(B)–OB(5)	84.4(2)
NA(1)–Co(A)–OA(6)	88.1(2)	NB(1)–Co(B)–OB(6)	87.8(2)
NA(2)–Co(A)–OA(8)	86.4(2)	NB(2)–Co(B)–OB(8)	87.0(2)
NA(1)–Co(A)–NA(2)	89.4(2)	NB(1)–Co(B)–NB(2)	89.8(2)
Co(A)–NA(1)–CA(1)	106.7(4)	Co(B)–NB(1)–CB(1)	106.0(4)
Co(A)–NA(1)–CA(3)	104.7(4)	Co(B)–NB(1)–CB(3)	105.8(5)
Co(A)–NA(1)–CA(5)	106.9(4)	Co(B)–NB(1)–CB(5)	108.3(5)
Co(A)–NA(2)–CA(2)	105.1(4)	Co(B)–NB(2)–CB(2)	105.1(4)
Co(A)–NA(2)–CA(7)	112.3(4)	Co(B)–NB(2)–CB(7)	113.6(4)
Co(A)–NA(2)–CA(9)	106.3(4)	Co(B)–NB(2)–CB(9)	105.7(4)
Co(A)–OA(5)–CA(4)	112.2(5)	Co(B)–OB(5)–CB(4)	113.5(5)
Co(A)–OA(6)–CA(6)	114.3(4)	Co(B)–OB(6)–CB(6)	115.8(4)
Co(A)–OA(8)–CA(10)	117.0(5)	Co(B)–OB(8)–CB(10)	115.1(5)
NA(1)–CA(1)–CA(2)	106.0(6)	NB(1)–CB(1)–CB(2)	107.0(6)
CA(1)–CA(2)–NA(2)	109.4(6)	CB(1)–CB(2)–NB(2)	109.9(6)
NA(1)–CA(3)–CA(4)	108.0(6)	NB(1)–CB(3)–CB(4)	107.2(7)

(continued overleaf)

TABLE III. *(continued)*

Atoms	Angles (°)	Atoms	Angles (°)
CA(3)–CA(4)–OA(1)	119.4(7)	CB(3)–CB(4)–OB(1)	119.7(8)
CA(3)–CA(4)–OA(5)	116.6(6)	CB(3)–CB(4)–OB(5)	115.2(7)
OA(1)–CA(4)–OA(5)	124.0(7)	OB(1)–CB(4)–OB(5)	125.1(8)
NA(1)–CA(5)–CA(6)	113.0(6)	NB(1)–CB(5)–CB(6)	110.8(6)
CA(5)–CA(6)–OA(2)	119.5(6)	CB(5)–CB(6)–OB(2)	120.1(7)
CA(5)–CA(6)–OA(6)	116.7(6)	CB(5)–CB(6)–OB(6)	116.7(6)
OA(2)–CA(6)–OA(6)	123.8(7)	OB(2)–CB(6)–OB(6)	123.2(7)
NA(2)–CA(9)–CA(10)	111.1(6)	NB(2)–CB(9)–CB(10)	111.1(6)
CA(9)–CA(10)–OA(4)	120.1(7)	CB(9)–CB(10)–OB(4)	121.2(7)
CA(9)–CA(10)–OA(8)	114.8(6)	CB(9)–CB(10)–OB(8)	116.5(7)
OA(4)–CA(10)–OA(8)	125.1(7)	OB(4)–CB(10)–OB(8)	122.3(7)
NA(2)–CA(7)–CA(8)	113.2(6)	NB(2)–CB(7)–CB(8)	116.1(6)
CA(7)–CA(8)–OA(3)	108.7(6)	CB(7)–CB(8)–OB(3)	111.0(8)
CA(7)–CA(8)–OA(7)	127.4(7)	CB(7)–CB(8)–OB(7)	124.9(8)
OA(3)–CA(8)–OA(7)	123.9(7)	OB(3)–CB(8)–OB(7)	124.1(9)

TABLE IV. Least-Squares Planes and Deviations of Atoms (Å) from Planes.

Plane	**Atom defining plane**	Equation of mean plane
R1A	Co(A), NA(1), CA(5), CA(6), OA(6)	$0.0840X - 0.8480Y - 0.5233Z + 2.7256 = 0$
R2A	Co(A), NA(2), CA(9), CA(10), OA(8)	$-0.6722X + 0.4556Y - 0.5836Z + 8.1356 = 0$
GA	Co(A), NA(1), CA(3), CA(4), OA(5)	$-0.8188X - 0.4663Y + 0.3349Z + 10.0948 = 0$
EA	Co(A), NA(1), NA(2)	$-0.6593X - 0.3305Y + 0.6754Z + 6.7222 = 0$
R1B	Co(B), NB(1), CB(5), CB(6), OB(6)	$-0.5312X + 0.7093Y - 0.4634Z + 2.9444 = 0$
R2B	Co(B), NB(2), CB(9), CB(10), OB(8)	$-0.8305X - 0.5194Y - 0.2010Z + 8.2452 = 0$
GB	Co(B), NB(1), CB(3), CB(4), OB(5)	$0.2748X - 0.1927Y - 0.9420Z + 8.2452 = 0$
EB	Co(B), NB(1), NB(2)	$0.2824X - 0.4902Y - 0.8246Z + 5.0594 = 0$

Atom	Plane R1A	Atom	Plane R2A	Atom	Plane GA	Atom	Plane EA
Co(A)	−0.037	Co(A)	0.080	Co(A)	0.251	Co(A)	0.000
NA(1)	0.061	NA(2)	−0.144	NA(1)	−0.267	NA(1)	0.000
CA(5)	−0.050	CA(9)	0.147	CA(3)	0.168	NA(2)	0.000
CA(6)	−0.036	CA(10)	−0.031	CA(4)	−0.001	CA(1)[a]	0.468
OA(6)	0.066	OA(8)	−0.046	OA(5)	−0.135	CA(2)[a]	−0.242
OA(2)[a]	−0.104	OA(4)[a]	−0.091	OA(1)[a]	0.044		
r.m.s. Δ	0.052	r.m.s. Δ	0.102	r.m.s. Δ	0.190	r.m.s. Δ	0.000

Atom	Plane R1B	Atom	Plane R2B	Atom	Plane GB	Atom	Plane EB
Co(B)	0.049	Co(B)	0.136	Co(B)	−0.103	Co(B)	0.000
NB(1)	−0.054	NB(2)	−0.141	NB(1)	0.198	NB(1)	0.000
CB(5)	0.026	CB(9)	0.111	CB(3)	−0.305	NB(2)	0.000
CB(6)	0.022	CB(10)	0.002	CB(4)	0.001	CB(1)[a]	−0.500
OB(6)	−0.041	OB(8)	−0.101	OB(5)	0.251	CB(2)[a]	0.178
OB(2)[a]	0.123	OB(4)[a]	0.031	OB(1)[a]	−0.032		
r.m.s. Δ	0.040	r.m.s. Δ	0.110	r.m.s. Δ	0.203	r.m.s. Δ	0.000

[a] These atoms were not used in the calculation of planes.

TABLE V. Intermolecular Hydrogen Bonding with Least-Squares Estimated Standard Deviations in Parentheses.[a]

D	H	A	D····A (Å)	D—H (Å)	H···A (Å)
OA(3)	H(25)	$OW(2)^{i}$	2.655(10)	0.93(12)	1.86(12)
OB(3)	H(26)	$OW(6)^{ii}$	2.881(11)	1.00(12)	1.88(12)
OW(A)	H(27)	OB(2)	2.570(8)	0.83(10)	1.74(10)
OW(A)	H(28)	$OW(3)^{iii}$	2.678(9)	0.73(12)	1.97(12)
OW(B)	H(29)	OW(6)	2.681(8)	0.74(11)	2.02(11)
OW(B)	H(30)	$OA(2)^{iv}$	2.654(7)	1.03(12)	1.64(12)
OW(1)	H(31)	$OA(1)^{iii}$	2.812(11)	1.05(12)	2.16(12)
OW(1)	H(32)	OW(4)	2.684(12)	1.14(12)	1.55(12)
OW(2)	H(33)	$OA(1)^{iv}$	2.793(9)	0.76(12)	2.11(12)
OW(2)	H(34)	$OA(2)^{v}$	2.823(9)	1.16(14)	1.69(14)
OW(2)	H(35)	OW(5)	2.713(12)	1.11(11)	1.63(12)
OW(3)	H(36)	OB(1)	2.787(10)	1.91(11)	1.94(11)
OW(4)	H(37)	OB(5)	2.874(10)	0.87(12)	2.09(12)
OW(4)	H(38)	$OB(4)^{vi}$	2.860(10)	1.11(13)	1.78(13)
OW(5)	H(39)	OB(8)	2.932(11)	0.88(11)	2.09(11)
OW(5)	H(40)	$OW(1)^{vii}$	2.750(13)	1.05(13)	1.71(13)
OW(6)	H(41)	OW(2)	2.972(9)	1.11(13)	1.89(13)
OW(6)	H(42)	$OB(4)^{vi}$	2.778(9)	0.94(12)	1.88(12)

[a] Atoms are related to those given in Table I as follows:

i	(0.5 – x, –y, –0.5 + z)	v	(–0.5 + x, 0.5 – y, –z)
ii	(0.5 – x, –y, 0.5 + z)	vi	(x, y, –1.0 + z)
iii	(0.5 – x, 1.0 – y, –0.5 + z)	vii	(x, y, 1.0 + z)
iv	(–0.5 + x, 0.5 – y, 1.0 – z)		

maximum peaks with opposite signs at 608 and 541 nm, where the absorption peaks of the single crystals coincide well with the reported peak positions of [Co(Hedta)H_2O] (551 and 381 nm) [18]. Unless the solution is made strongly acidic, the CD spectrum changes gradually towards that of the $[Co(edta)]^-$ anion [19].

Description of the Structure

Intramolecular bond distances and bond angles, with least-squares estimated standard deviations, are listed in Tables II and III. Least-squares planes and deviations of atoms from these planes are given in Table IV. Intermolecular hydrogen bondings are listed in Table V. A perspective view of 'complex-A' which contains the Co(A) atom and a stereoview of 'complex-B' which contains the Co(B) atom are shown in Figs. 1a and 1b respectively. The contents of one unit cell showing hydrogen bonding are illustrated in Fig. 2. In these figures, the thermal ellipsoids have been drawn to include 50% of the probability distribution. In Fig. 2, all hydrogen atoms and all atoms belonging to the neighboring unit cell have been omitted for clarity. The crystal structure is composed of two crystallographically independent complexes of the same absolute configuration ('complex-A' and 'complex-B') and water molecules. The ethylenediaminetriacetatoacetic acid ligand is pentadentate with one free acetate group protonated (–CH_2COOH) and with a water molecule occupying the sixth position, thus forming a six-coordinated complex with the Co(III) ion (Fig. 1a and 1b). Averages of chemically-equivalent bond distances around the Co(A) and Co(B) atoms are as follows; Co–N1, 1.931(8) Å: Co–N2, 1.982(6) Å: Co–O(R1), 1.881(22) Å: Co–O(R2), 1.880(1) Å: Co–O(G), 1.911(4) Å: Co–OW, 1.928(1) Å, where O(R1), O(R2), and O(G) mean the coordinated oxygen atoms in R1, R2, and G chelate rings, respectively (see Figs. 1a and 1b). The Co–N1 bonds are much shorter than the Co–N2 bonds and also than the Co–N bonds in other compounds, for example, Λ-[Co(sen)]Cl. d-tart·$6H_2O$, 1.971(6) Å [20] and Λ-$[Co(en)_3]$Cl·d-tart·$5H_2O$, 1.964(3) Å [21]. A Co–N bond of this length has already been found in NH_4[Co(edta)]·$2H_2O$ (1.925(5) Å [2]: the difference may be caused by the strain of chelate rings (see below). The Co–OW bonds are notably long compared with the Co–OH_2 bonds of, *e.g.*, 1.873(5) Å in $Cs[Co(H_2O)_6](SO_4)_2 \cdot 6H_2O$ [22]. All bond distances and bond angles around the CA(8) and CB(8) atoms indicate that the OA(3) and OB(3) atoms in free acetate groups are protonated (see Tables II and III). The other bond distances and bond angles are in good agreement with the values reported previously [2, 10, 23, 24].

The strain in the complex may be expressed by the deviation from planarity of three kinds of glyci-

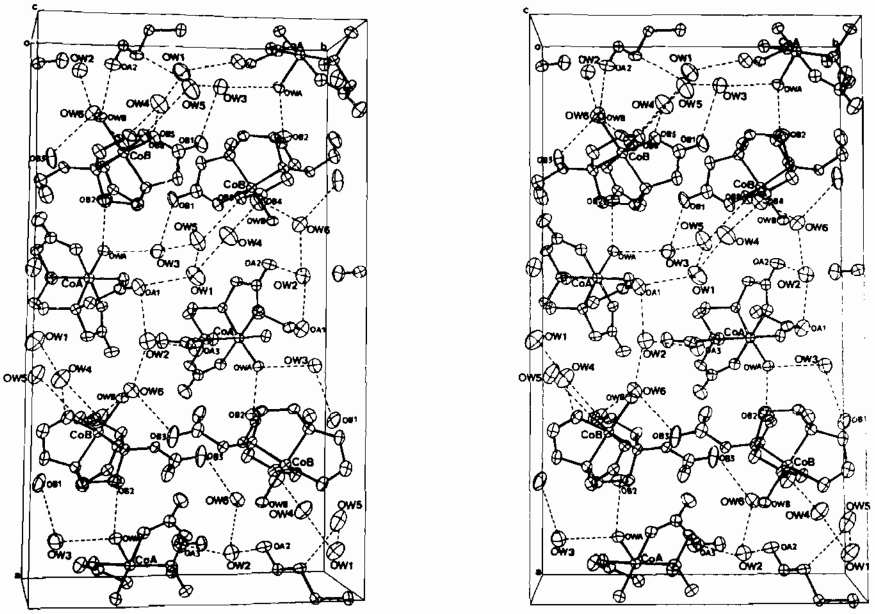

Fig. 2. A stereoview of the contents of one unit cell showing hydrogen bondings (-----).

nato rings (R1, R2, and G), as pointed out by Hoard *et al.* for the $[Co(edta)]^-$ anion [2]; an unstrained glycinato ring should be planar. As shown in Table IV, the degree of strain decreases in the order G-ring > R2-ring > R1-ring in both 'complex-A' and 'complex-B'. This order is consistent with the general trend that G-rings are highly strained compared with R-rings in other edta (or Hedta) complexes [2, 10, 23]. All the acetate skeletons are almost planar, so that the least-squares planes for these are not listed in Table IV.

The conformation of the free $-CH_2-COOH$ arm is expressed by two Co–N2–C7–C8 and N2–C7–C8–O7 torsional angles. As described below, the conformation of two $-CH_2-COOH$ arms in 'complex-A' and 'complex-B' are almost the same. The Co(A)–NA(2)–CA(7)–CA(8) and Co(B)–NB(2)–CB(7)–CB(8) torsional angles are 176.1° and 178.9°, respectively. These values mean that the C8 atom is located almost nearly *trans* to the Co atom. The NA(2)–CA(7)–CA(8)–OA(7) and NB(2)–CB(7)–CB(8)–OB(7) torsional angles are −11.6° and 2.7°, respectively. These values mean that the N2 atom is located approximately *cis* to the O7 atom which takes part in the C=O double bond. Thus, the overall conformation is such that Co and C8 are mutually *trans* and N2 and O7 are *cis*. This conformation is energetically most stable in a complex without the influence of crystal lattices, and it is also found in $[Rh(Hedta)H_2O]$ (Rh–N–C–C = 177.4° and N–C–C–O = −14.8°) [10]. Thus, the most stable conformation in $[M(Hedta)H_2O]$ is found in common with all the complexes of the $[M(Hedta)H_2O]$ type, which suggests that in solution the $[M(Hedta)H_2O]$ complex presumably exists in this conformation. As a result, the reason for only the Co salt being resolved spontaneously does not seem to be attributable to the molecular structure of the complex, including the conformation of the free $-CH_2-COOH$ arm.

Hydrogen Bonding and the Packing Mode

Six crystallographically-independent water molecules are all tetrahedrally surrounded through hydrogen bonding and bound quite tightly in the crystal lattice (Fig. 2). The manner of the hydrogen bonding in 'complex-A' is analogous to that in 'complex-B'. Each free $-CH_2-COOH$ arm is involved in hydrogen bonding with one water molecule (OA(3)–H(25)···OW(2) or OB(3)–H(26)···OW(6)). Each coordinated water molecule, OW(A) or OW(B), is linked to one water molecule (OW(A)–H(28)···OW(3) or OW(B)–H(29)···OW(6)) and one uncoordinated oxygen atom in the neighboring complex (OW(A)–H(27)···OB(2) or OW(B)–H(30)···OA(2)). the latter is the only hydrogen bonding between the complexes and forms infinite 2_1 spiral chains parallel to the a axis. A closer inspection of this 2_1 spiral chains reveals that two independent complexes, 'complex-A' and 'complex-B' are disposed so as to make pseudo-4_1 right-handed spiral chains, with the complexes rotating by 90°/step around the 2_1 screw axes. The features of these homochiral pseudo-4_1 spiral chains are illustrated in Fig. 3 as the stereopairs.

Now, we compare the crystal structures of active $[Co(Hedta)H_2O]\cdot 3H_2O$ and racemic $[M(Hedta)H_2O]$

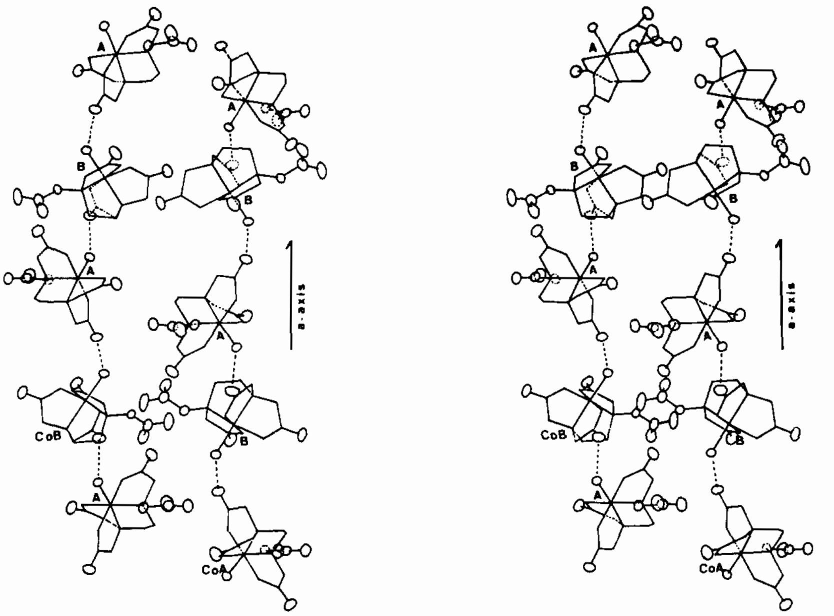

Fig. 3. A stereoview illustrating the homochiral pseudo-4_1 spiral chains.

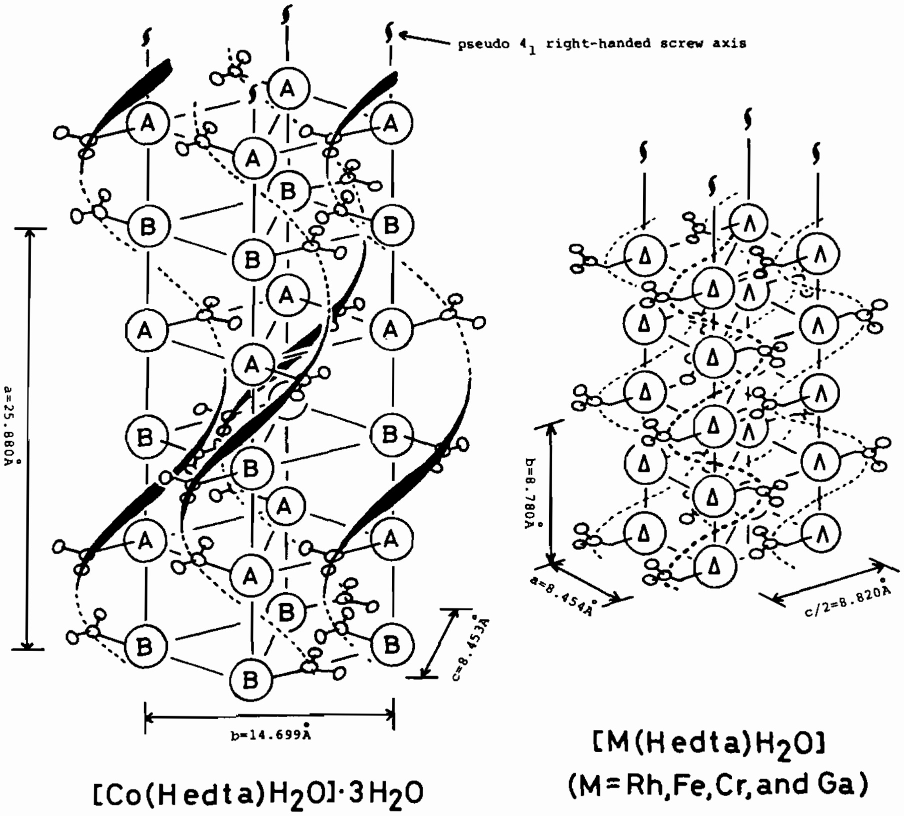

Fig. 4. The schematic representation of the crystal structures in Λ(R,R)Δ(G,R)-[Co(Hedta)H_2O]·$3H_2O$ and racemic-[M(Hedta)-H_2O] (M = Rh, Fe, Cr, and Ga), with the cell constants for the Co and Rh salts.

(M = Rh, Fe, Cr, and Ga). Figure 4 shows the schematic representation of the crystal structures in the Co and Rh salts. In the case of the Rh salt, there is no water of crystallization so that the free $-CH_2-COOH$ arm and the coordinated H_2O are both involved in intermolecular hydrogen bonding. In an analogous way to the Co salt, the coordinated H_2O is linked to one uncoordinated oxygen atom in the neighboring complex, forming an infinite 2_1 spiral chain with an 8.780 Å period parallel to the b axis. By the side of the 2_1 spiral chain formed by the Δ-complexes, another 2_1 spiral chain composed of the Δ-complexes and the 2_1 spiral chain of the Λ-complexes are arranged, 8.454 Å and 8.820 Å apart, respectively. In this crystal structure it seems that no chiral discrimination between those spiral chains can be performed since a 2_1 spiral chain itself has no chirality at all. In the case of the Co salt, the pseudo-4_1 right-handed spiral chains are formed with a 25.880 Å period, instead of the simple 2_1 spiral chains in the Rh salt. By the side of one pseudo-4_1 right-handed spiral chain, the other two spiral chains are placed at the distances of 8.453 Å and 8.487 Å, and they are fitted in two modes. For these pseudo-4_1 right-handed spiral chains to fit with one another (see Figs. 3), they must be composed of only one enantiomer, and therefore the formation of such a chiral spiral chain results in chiral discrimination in the crystal structure of this complex.

Previously, with respect to the crystal structures of $K_3[Co(ox)_3]\cdot nH_2O$, we proposed the following interpretation: in the optically active crystals, a three-dimensional chiral discrimination occurs by forming a chiral 3_1 (or 3_2) spiral chain composed of the $[Co(ox)_3]^{3-}$ anion and the K^+ cation, while only one-dimensional zigzag chains are formed in racemic crystals. In this work the mode of chiral discrimination in $[Co(Hedta)H_2O]\cdot 3H_2O$ is also interpreted by the compact fitting between chiral spiral chains.

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