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Crystal Structures of the Racemic Tartrate and the Two *d*-Tartrate Salts of the Tris(ethylenediamine)cobalt(III) Complex

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The crystal structures of Δ,Λ-[Co(en)$_3$]$_2$(*d,l*-tart)$_3\cdot$10H$_2$O (I), Λ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$19H$_2$O (II), and Δ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$11.5H$_2$O (III) (en = 1,2-diaminoethane; tart = tartrate dianion) have been determined by single-crystal structure analysis. Crystal data are as follows: I is monoclinic, with space group $P2_1/n$, $Z = 4$, $a = 22.405$ (5) Å, $b = 17.881$ (3) Å, $c = 12.067$ (5) Å, $\beta = 93.41$ (2)°, $R = 0.074$, and 4428 reflections; II is orthorhombic, with space group $P2_12_12_1$, $Z = 4$, $a = 24.810$ (4) Å, $b = 19.015$ (3) Å, $c = 12.849$ (2) Å, $R = 0.066$, and 3348 reflections; III is triclinic, with space group $P1$, $Z = 1$, $a = 14.153$ (3) Å, $b = 12.145$ (2) Å, $c = 8.505$ (2) Å, $\alpha = 106.51$ (1)°, $\beta = 96.10$ (1)°, $\gamma = 81.54$ (1)°, $R = 0.055$, and 3785 reflections. A characteristic feature common to these three crystals is that they are considered to be a pile of blocks composed of the complex and tartrate ions. Face-to-face close contact was found not only between the triangular facet of three NH$_2$ groups of the Λ-complex ion and a set of four oxygen atoms of the *d*-tartrate ion (and between the Δ-complex ion and *l*-tartrate ion) in crystals of I and II, which is commonly found in some analogous crystals, but also between the Δ-complex ion and *d*-tartrate ion (and between the Λ-complex ion and *l*-tartrate ion) in crystals of I and III. The latter combinations (Δ–*d* and Λ–*l*) were found only in the overlapping parts of adjacent blocks and presumed to play a role in strengthening the connection of these blocks.

Introduction

In the preceding paper the crystal structure analyses of Δ,Λ-[Ni(en)$_3$](*d,l*-tart)$\cdot$H$_2$O and Δ-[Ni(en)$_3$]$_{1.5}$(*d*-tart)$_{1.5}\cdot$2H$_2$O (*d*-C$_4$H$_4$O$_6$$^{2-}$, hereafter abbreviated as the *d*-tart^{2-} ion) were shown to reveal a face-to-face ion-pair structure in the Λ–d and Δ–*l* combinations, but not in the Λ–*l* and Δ–*d* combinations.[1] Thus, the Λ–*d* and Δ–*l* face-to-face ion pairs were concluded to be energetically more favorable than the Λ–*l* and Δ–*d* ion pairs. One may ask whether such a situation applies to the combination of [Co(en)$_3$]$^{3+}$ and tart^{2-} ions too, and the present study was undertaken to answer this question. Thus, the crystal structure analyses of three salts, Δ,Λ-[Co(en)$_3$]$_2$(*d,l*-tart)$_3\cdot$10H$_2$O, Λ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$19H$_2$O, and Δ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$11.5H$_2$O, were undertaken.

Experimental Section

Preparation. (a) Δ,Λ-[Co(en)$_3$]$_2$(*d,l*-tart)$_3\cdot$10H$_2$O. Five grams of racemic tartaric acid was neutralized with 5.6 g of sodium bicarbonate in 20 mL of water. The solution was concentrated to obtain crystals of the sodium salt of racemic tartrate. [Co(en)$_3$]Cl$_3\cdot$3H$_2$O was prepared according to the literature method.[2] Two grams of [Co(en)$_3$]Cl$_3\cdot$3H$_2$O was dissolved in 20 mL of water. To this solution was added 1.5 g of the Na$_2$(*d,l*-tart) salt dissolved in 30 mL of water. After this solution was allowed to stand for several days, orange needlelike crystals were deposited. A crystal of a suitable size was selected for the X-ray crystal analysis. Anal. Calcd for [Co(en)$_3$]$_2$(*d,l*-tart)$_3\cdot$10H$_2$O: C, 26.14; H, 7.31; N, 15.24. Found: C, 25.91; H, 7.12; N, 15.46.

(b) Λ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$19H$_2$O. Λ-[Co(en)$_3$]Cl(*d*-tart)$\cdot$5H$_2$O was obtained according to the literature method.[2] Two-tenths gram of this salt was dissolved in 10 mL of water. The solution obtained was allowed to pass through a column packed with the *d*-tart^{2-} form of QAE-Sephadex (50-cm length × 1-cm diameter), and the eluate was concentrated until crystals appeared. The crystals thus obtained were dissolved in water, and the solution was allowed to stand for several days at room temperature. Orange needlelike crystals were obtained, and a single crystal of suitable size was selected for the X-ray crystal analysis. The crystals lost their water of crystallization so easily that elemental analysis was not attempted, and the sample crystal was sealed in a glass capillary.

(c) Δ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$11.5H$_2$O. Δ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$11.5H$_2$O was obtained in the same manner as in (b), starting with Δ-[Co(en)$_3$]I$_3$ instead of Λ-[Co(en)$_3$]Cl(*d*-tart)$\cdot$5H$_2$O. Orange crystals were obtained, but since they also readily lost their water of crystallization, elemental analysis was not attempted and the sample crystal was sealed in a capillary.

X-ray Measurements. The cell dimensions and space group symmetries were preliminarily checked by Weissenberg photographs by using Ni Kα radiation. The systematic absences of reflections suggested the following possible space groups: $P2_1/n$ for Δ,Λ-[Co(en)$_3$]$_2$(*d,l*-tart)$_3\cdot$10H$_2$O (I); $P2_12_12_1$ for Λ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$19H$_2$O (II); $P1$ or $P\bar{1}$ for Δ-[Co(en)$_3$]$_2$(*d*-tart)$_3\cdot$11.5H$_2$O (III), $P\bar{1}$ being eliminated because of the chirality of the compound. Determination of cell constants and collection of intensity data were carried out on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Unit cell constants were determined by the least-squares refinement of 25 reflections for each compound. The crystals selected for data collection had the following approximate dimensions: 0.2 × 0.2 × 0.3, 0.2 × 0.2 × 0.3, and 0.3 × 0.3 × 0.3 mm for I–III, respectively. Intensity data were collected at room temperature (22 °C) by an ω–2θ scan mode from $2\theta = 3°$ up to $2\theta = 55$, 55, and 50°, for I–III, respectively. The numbers of reflections collected were 7321 ($+h,+k,\pm l$), 5531 ($+h,+k,+l$) and 4077 ($+h,\pm k,\pm l$) for I–III, respectively. Standard Lp corrections were applied, but no corrections for the absorption effect were made (μ(Mo Kα) = 7.8, 6.4, and 6.9 cm^{-1} for I–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. Several cycles of the block-diagonal least-squares refinement reduced the R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) to 0.075, 0.067, and 0.057 for I–III, respectively. At this stage, the positions of the hydrogen atoms bonded to N and C atoms were calculated (assuming 1.0 Å for both N–H and C–H bond distances and the tetrahedral configuration for both N and C atoms). The positions of the hydrogen atoms of a water molecule were also calculated on the basis of the following assumption: When the hydrogen atom of a water molecule is hydrogen-bonded to the oxygen atom of the carboxyl group of the tart^{2-} ion, the hydrogen atom in question is assumed to be 1.0 Å distant from the oxygen atom of the water molecule.[3] The final refinement including these H atoms with isotropic temperature factors converged the R value to 0.074, 0.066, and 0.054 for I–III, respectively. In the refinement, the quantity minimized was $w(|F_o| - k|F_c|)^2$. The weighting scheme used was $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics for each reflection; the a and b values chosen were 0.2 and 0.0009, respectively. The atomic scattering factors for non-hydrogen atoms were taken from ref 4. The absolute configurations of the II and III were deduced from the comparison with those of the *d*-tartrate anion. All the computations were carried out on a HITAC computer at the Hiroshima University Information Processing Center. The computer programs used were UNICS-III[5] and ORTEP.[6]

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(1) Mizuta, T.; Kushi, Y.; Yoneda, H. *Inorg. Chim. Acta* **1987**, *132*, 11.

(2) Werner, A. *Ber.* **1912**, *45*, 121.

(3) The number of waters of crystallization in sample crystals were determined by the TG (thermogravimetric) method: 9.4 for I, 19.0 for II, and 11.4 for III. The present X-ray analyses for crystals I and III revealed that the number of water molecules is 10 for I and 11.5 for III, in good agreement with the TG results. However, considerably disordered character was found concerning the location of water molecules in crystal II at the refinement step. The number of water molecules whose positions could be determined is only 9 out of 19 in crystal II. As to the remaining 10 water molecules, their electron density was spread out so much that their positions could not be determined.

(4) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 71.

(5) Ashida, T. In *The Universal Crystallographic Computation Program System*; Sakurai, T., Ed.; The Crystallographic Society of Japan: Tokyo, 1979.

0020-1669/88/1327-3836$01.50/0

Table I. Summary of Crystal Data and Refinement Conditions for Three Kinds of Crystals

	I	II	III
formula	$(C_6H_{24}CoN_6)_2$-$(C_4H_4O_6)_3\cdot 10H_2O$	$(C_6H_{24}CoN_6)_2$-$(C_4H_4O_6)_3\cdot 19H_2O$	$(C_6H_{24}CoN_6)_2$-$(C_4H_4O_6)_3\cdot 11.5H_2O$
a, Å	22.405 (5)	24.810 (4)	14.153 (3)
b, Å	17.881 (3)	19.015 (3)	12.145 (2)
c, Å	12.067 (5)	12.849 (2)	8.505 (2)
α, deg			106.51 (1)
β, deg	93.41 (2)		96.10 (1)
γ, deg			81.54 (1)
vol, Å^3	4825 (2)	6061 (1)	1380 (4)
Z	4	4	1
fw	1102.83	1264.96	1129.85
space group	$P2_1/n$	$P2_12_12_1$	$P1$
ρ_{obsd}, g cm^{-3}	1.54	1.44	1.46
ρ_{calcd}, g cm^{-3}	1.52	1.39	1.36
μ, cm^{-1}	7.80	6.40	6.87
no. of reflcns collcd	7321	5531	4077
no. of reflcns, used ($\lvert F_o\rvert > 3\sigma\lvert F_o\rvert$)	4428	3348	3785
final R value[a]	0.074	0.066	0.055
final R_w value[b]	0.133	0.097	0.075

[a] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [b] $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$.

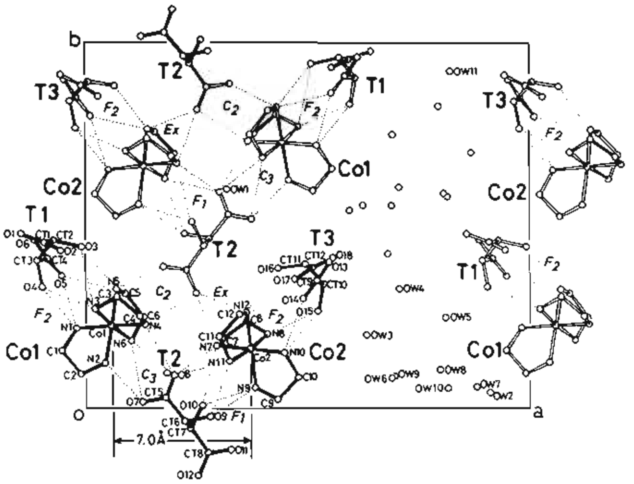

Figure 1. Drawing of part of the components (c = 0–$^1/_2$) viewed along the c axis with the numbering scheme for Δ,Λ-[Co(en)$_3$]$_2$(d,l-tart)$_3$·10H$_2$O. Hydrogen bonds are indicated by broken lines. Italic symbols, F_1, F_2, C_2, C_3, and E_x, represent the modes of hydrogen bonds (see text).

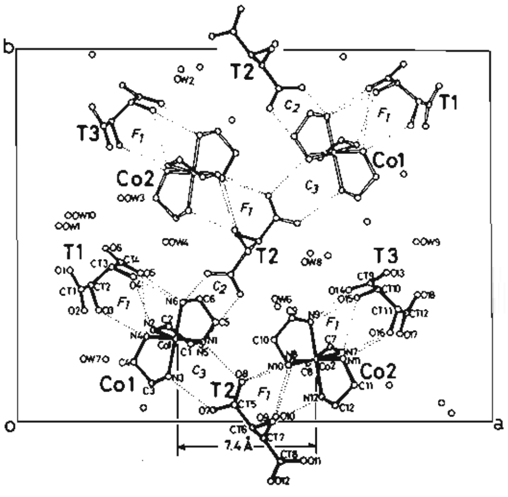

Figure 2. Drawing of part of the components (c = $^1/_2$–1) viewed along the c axis with the numbering scheme for Λ-[Co(en)$_3$]$_2$(d-tart)$_3$·19H$_2$O. Hydrogen bonds are indicated by broken lines. Italic symbols, F_1, C_2, and C_3, represent the modes of hydrogen bonds (see text).

Table II. Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) for Δ,Λ-[Co(en)$_3$]$_2$(d,l-tart)$_3$·10H$_2$O

atom	x	y	z	B_{EQV}
Co1	579 (1)	2268 (1)	3089 (1)	2.1
Co2	3694 (1)	1640 (1)	3186 (1)	2.1
N1	−198 (4)	2197 (4)	2280 (6)	2.8
N2	430 (4)	1248 (4)	3588 (6)	2.8
N3	217 (3)	2723 (5)	4376 (6)	2.9
N4	1334 (4)	2311 (5)	3992 (7)	3.1
N5	698 (4)	3256 (4)	2422 (7)	3.1
N6	1008 (3)	1874 (4)	1848 (6)	2.8
N7	2943 (3)	1729 (4)	2241 (6)	2.7
N8	4088 (4)	2042 (5)	1875 (6)	3.0
N9	3807 (4)	584 (5)	2734 (6)	2.9
N10	4464 (3)	1532 (5)	4017 (6)	2.8
N11	3226 (4)	1298 (4)	4427 (6)	2.8
N12	3614 (4)	2644 (4)	3793 (7)	3.1
C1	−539 (5)	1581 (6)	2759 (9)	3.6
C2	−111 (4)	950 (5)	2943 (9)	3.2
C3	706 (5)	3053 (6)	5109 (8)	3.4
C4	1212 (5)	2527 (7)	5166 (8)	3.9
C5	888 (5)	3157 (6)	1273 (9)	3.8
C6	1298 (5)	2503 (7)	1264 (9)	3.7
C7	3077 (4)	1911 (6)	1091 (8)	3.2
C8	3618 (5)	2395 (6)	1130 (8)	3.2
C9	4308 (5)	264 (6)	3426 (8)	3.4
C10	4774 (5)	860 (6)	3601 (8)	3.4
C11	3000 (5)	1973 (6)	5022 (9)	3.7
C12	3455 (5)	2581 (6)	4983 (8)	3.3
CT1	−912 (6)	4553 (7)	4877 (9)	4.7
CT2	−708 (6)	4603 (7)	3648 (10)	4.9
CT3	−1067 (5)	4049 (7)	2989 (11)	5.0
CT4	−842 (7)	4097 (9)	1748 (10)	6.3
CT5	1788 (4)	302 (5)	3065 (8)	2.7
CT6	2213 (4)	−355 (5)	3037 (8)	2.6
CT7	2341 (4)	−545 (5)	1838 (8)	2.3
CT8	2735 (5)	−1212 (6)	1796 (8)	3.2
CT9	5199 (6)	3510 (7)	4481 (9)	4.8
CT10	5341 (5)	3415 (6)	3183 (10)	3.9
CT11	4938 (6)	3958 (6)	2564 (10)	4.4
CT12	5088 (6)	3853 (7)	1326 (9)	4.9
O1	−1428 (6)	4783 (7)	4985 (8)	8.4
O2	−547 (5)	4333 (6)	5621 (6)	6.9
O3	−83 (3)	4424 (4)	3553 (6)	4.3
O4	−959 (3)	3328 (4)	3449 (6)	3.7
O5	−529 (5)	3632 (6)	1387 (8)	6.9
O6	−1135 (4)	4611 (5)	1205 (7)	5.4
O7	1263 (3)	186 (4)	2708 (7)	4.3
O8	1978 (3)	922 (4)	3408 (7)	4.3
O9	2771 (3)	−222 (4)	3627 (5)	3.4
O10	2610 (3)	101 (4)	1371 (6)	3.2
O11	3249 (3)	−1118 (5)	1473 (7)	5.2
O12	2517 (3)	−1829 (4)	2088 (7)	4.2
O13	5470 (4)	4008 (5)	4987 (6)	5.7
O14	4884 (4)	3015 (5)	4877 (6)	5.8
O15	5221 (3)	2674 (4)	2818 (6)	3.3
O16	4333 (3)	3836 (4)	2800 (6)	4.2
O17	4701 (5)	3547 (6)	714 (7)	6.6
O18	5551 (4)	4133 (5)	1063 (7)	5.5
OW1	6823 (4)	3997 (6)	5051 (10)	7.8
OW2	−926 (6)	435 (7)	377 (11)	9.3
OW3	6309 (4)	2018 (7)	3067 (11)	8.6
OW4	7050 (5)	3279 (7)	3103 (10)	9.3
OW5	8091 (4)	2494 (7)	2972 (11)	8.4
OW6	6876 (8)	824 (10)	4255 (15)	14.5
OW7	8771 (7)	598 (11)	4880 (12)	14.7
OW8	7951 (10)	1058 (14)	3381 (20)	8.6
OW9	3060 (11)	−889 (13)	−1325 (19)	8.5
OW10	1871 (13)	−559 (18)	−1661 (26)	12.5
OW11	8214 (14)	−762 (19)	3532 (29)	14.3

Results

Description of the Crystal Structures. The crystallographic data and the conditions for the structure analyses are summarized in Table I. Among the final values of the atomic coordinates, only

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(6) Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table III. Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) for Λ-[Co(en)$_3$]$_2$(*d*-tart)$_3$·19H$_2$O

atom	*x*	*y*	*z*	B_{EQV}
Co1	3315 (1)	2214 (1)	6945 (1)	2.8
Co2	6287 (1)	1665 (1)	7952 (1)	2.5
N1	3890 (4)	2134 (5)	8001 (9)	3.1
N2	2846 (4)	2429 (5)	8111 (10)	3.5
N3	3155 (4)	1203 (5)	7000 (11)	3.7
N4	2708 (5)	2258 (6)	5979 (8)	3.3
N5	3855 (5)	2050 (6)	5826 (10)	4.1
N6	3470 (4)	3197 (5)	6728 (8)	3.2
N7	6825 (4)	1854 (5)	6907 (9)	3.2
N8	5789 (4)	1623 (6)	6758 (7)	2.9
N9	6168 (4)	2678 (5)	8147 (8)	2.7
N10	5694 (4)	1524 (5)	8943 (7)	2.8
N11	6847 (5)	1690 (7)	9043 (9)	3.9
N12	6404 (4)	651 (5)	7903 (9)	3.1
C1	3620 (7)	2072 (9)	9026 (12)	4.8
C2	3164 (8)	2547 (9)	9083 (12)	5.0
C3	2821 (7)	1007 (7)	6081 (13)	4.3
C4	2432 (7)	1581 (10)	5952 (12)	4.9
C5	4157 (7)	2662 (8)	5688 (11)	4.2
C6	3817 (8)	3281 (9)	5798 (11)	5.1
C7	6585 (6)	1997 (7)	5919 (10)	3.3
C8	6107 (6)	1557 (7)	5794 (9)	3.4
C9	5785 (6)	2782 (8)	9082 (11)	3.9
C10	5398 (6)	2200 (8)	9045 (11)	3.8
C11	7092 (8)	983 (10)	9134 (15)	5.6
C12	6673 (9)	436 (8)	8847 (15)	5.3
CT1	1321 (8)	3522 (9)	8471 (12)	5.0
CT2	1527 (6)	3623 (7)	7363 (10)	3.6
CT3	1986 (7)	4116 (7)	7311 (10)	3.6
CT4	2163 (7)	4240 (7)	6198 (11)	3.8
CT5	4542 (6)	455 (7)	7436 (12)	3.8
CT6	4926 (7)	−168 (7)	7640 (11)	3.8
CT7	5153 (6)	−428 (7)	6619 (12)	3.9
CT8	5519 (5)	−1062 (6)	6808 (10)	3.1
CT9	7437 (7)	3710 (7)	8931 (11)	3.9
CT10	7595 (5)	3549 (6)	7786 (10)	3.2
CT11	8019 (6)	3012 (8)	7750 (11)	3.9
CT12	8186 (6)	2904 (7)	6592 (10)	3.8
O1	1097 (6)	4031 (7)	8874 (10)	3.7
O2	1392 (6)	2952 (7)	8900 (10)	6.7
O3	1696 (4)	2970 (4)	6896 (8)	4.2
O4	2428 (4)	3860 (4)	7939 (8)	3.9
O5	2580 (4)	3960 (5)	5838 (7)	4.1
O6	1849 (5)	4616 (6)	5651 (9)	5.3
O7	4098 (4)	317 (5)	6990 (11)	5.3
O8	4704 (4)	1067 (5)	7675 (9)	4.8
O9	5360 (4)	5 (5)	8340 (8)	4.0
O10	5429 (5)	131 (5)	6126 (9)	4.5
O11	6004 (5)	−1032 (6)	6537 (9)	5.0
O12	5318 (4)	−1586 (5)	7180 (8)	4.2
O13	7782 (5)	4006 (7)	9479 (10)	5.9
O14	6977 (4)	3535 (6)	9236 (8)	4.8
O15	7150 (4)	3326 (5)	7183 (7)	3.5
O16	7849 (4)	2390 (5)	8224 (7)	3.9
O17	8057 (6)	2355 (6)	6161 (8)	5.6
O18	8428 (6)	3407 (6)	6169 (9)	6.1
OW1	871 (7)	5219 (9)	5795 (13)	8.4
OW2	3450 (5)	−551 (6)	8313 (10)	5.7
OW3	2178 (5)	5975 (6)	8718 (10)	5.7
OW4	3116 (4)	4805 (5)	8735 (7)	4.0
OW5	2630 (6)	358 (7)	8678 (10)	5.8
OW6	5476 (5)	3087 (6)	6432 (9)	4.9
OW7	1848 (6)	1655 (7)	8627 (9)	6.1
OW8	6161 (6)	4520 (7)	9756 (11)	6.4
OW9	8414 (8)	4840 (9)	6592 (14)	9.6
OW10	1076 (8)	5490 (10)	8577 (14)	8.9

Table IV. Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) for Δ-[Co(en)$_3$]$_2$(*d*-tart)$_3$·11.5H$_2$O

atom	*x*	*y*	*z*	B_{EQV}
Co1	0 (1)	10000 (1)	10000 (2)	2.3
Co2	6782 (1)	5908 (1)	1065 (2)	2.4
N1	−115 (6)	9562 (7)	12027 (9)	2.9
N2	703 (6)	8456 (7)	9231 (10)	2.8
N3	−1239 (5)	9445 (6)	9108 (10)	2.7
N4	40 (6)	10249 (6)	7830 (10)	2.9
N5	−634 (6)	11571 (6)	10963 (9)	2.5
N6	1209 (6)	10660 (7)	10771 (10)	3.3
N7	7991 (6)	5212 (6)	1921 (9)	2.8
N8	6797 (6)	7076 (6)	3195 (9)	2.9
N9	7456 (6)	6817 (7)	49 (9)	2.9
N10	5606 (6)	6731 (8)	266 (11)	3.7
N11	6826 (6)	4620 (7)	−950 (10)	3.2
N12	6021 (7)	4980 (8)	1881 (11)	3.7
C1	127 (9)	8287 (9)	11662 (12)	3.8
C2	950 (8)	7954 (9)	10652 (13)	3.6
C3	−1564 (9)	9866 (9)	7661 (13)	3.8
C4	−718 (9)	9689 (9)	6703 (12)	3.9
C5	101 (8)	12271 (10)	12085 (14)	4.0
C6	1020 (8)	11916 (9)	11236 (15)	4.0
C7	8404 (8)	6104 (9)	3313 (13)	3.4
C8	7589 (8)	6751 (9)	4324 (11)	3.5
C9	6763 (8)	7369 (10)	−1048 (12)	3.7
C10	5844 (8)	7727 (10)	−226 (14)	4.2
C11	6459 (11)	3637 (10)	−669 (16)	5.2
C12	5685 (10)	4021 (11)	484 (17)	5.3
CT1	−2781 (8)	13084 (8)	14089 (13)	3.7
CT2	−2473 (7)	11861 (7)	14188 (11)	2.8
CT3	−2953 (7)	11001 (8)	12761 (11)	2.8
CT4	−2692 (7)	9775 (9)	12878 (12)	3.2
CT5	2745 (8)	9065 (11)	7636 (14)	4.3
CT6	3626 (8)	8809 (11)	6606 (15)	4.3
CT7	3518 (9)	7654 (11)	5189 (15)	4.5
CT8	4426 (11)	7325 (14)	4238 (17)	6.3
CT9	9383 (7)	3310 (8)	−1817 (12)	3.1
CT10	9754 (7)	4472 (8)	−1600 (11)	3.1
CT11	9308 (7)	4946 (8)	−3000 (11)	2.8
CT12	9625 (8)	6136 (8)	−2798 (12)	3.1
O1	−3624 (7)	13423 (7)	14184 (15)	6.7
O2	−2148 (7)	13643 (7)	13922 (10)	5.3
O3	−1472 (5)	11493 (6)	14154 (8)	3.7
O4	−2684 (5)	11151 (6)	11276 (8)	3.2
O5	−2116 (5)	9086 (6)	11945 (10)	3.9
O6	−3095 (6)	9507 (7)	13965 (11)	4.7
O7	2230 (7)	9958 (9)	7696 (13)	6.5
O8	2674 (8)	8362 (9)	8376 (12)	6.4
O9	3717 (7)	9699 (9)	5917 (14)	6.5
O10	2687 (6)	7847 (9)	4214 (10)	5.9
O11	4330 (10)	7406 (17)	2805 (15)	11.6
O12	5182 (6)	7022 (9)	4939 (12)	5.8
O13	9720 (6)	2481 (6)	−2964 (9)	4.0
O14	8805 (6)	3231 (7)	−886 (11)	4.8
O15	9527 (5)	5278 (6)	−103 (8)	3.5
O16	8283 (5)	5027 (6)	−3010 (8)	3.6
O17	9065 (6)	6999 (6)	−2360 (11)	4.7
O18	10484 (7)	6099 (8)	−3071 (11)	5.2
OW1	991 (10)	5156 (13)	2033 (16)	9.4
OW2	1557 (9)	189 (10)	4143 (13)	8.2
OW3	1643 (14)	4247 (13)	4938 (20)	12.0
OW4	1554 (10)	2386 (10)	6187 (17)	8.9
OW5	5484 (8)	503 (12)	5981 (14)	8.3
OW6	3430 (11)	9368 (14)	1702 (17)	10.4
OW7	915 (9)	7271 (14)	4887 (16)	9.4
OW8	5450 (10)	5319 (9)	6539 (13)	8.2
OW9	3488 (15)	6145 (15)	8669 (23)	13.1
OW10	4189 (11)	1174 (16)	882 (20)	11.6
OW11	5816 (8)	589 (14)	9289 (14)	9.5
OW12	3019 (18)	2451 (25)	8650 (41)	10.1

those for the heavy atoms are listed in Tables II–IV. The coordinates for the hydrogen atoms are summarized in Tables SI–SIII.[7] The projections of the crystal structures of I(racemic), II(Λ–*d*), and III(Δ–*d*) along the *c*, *c*, and *b* axes, respectively, are shown in Figures 1–3, where the numbering scheme of the complex ions and the tart^{2-} ions is indicated. In these three projections, crystallographically asymmetric units are depicted as those whose bonds are shown in black. The projections of the crystal structures of the three salts, I–III, along the *b*, *b*, and *c* axes, respectively, are shown in Figures S1–S3.[7] As can be seen clearly, especially in Figure S2, these crystals have many vacant cavities in which water molecules are presumed to occur. The bond distances and

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(7) Supplementary material.

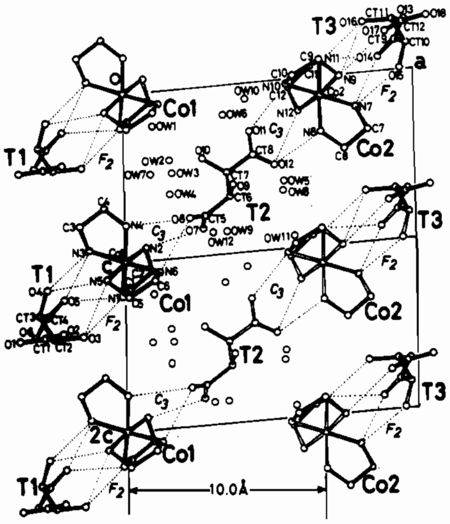

Figure 3. Drawing of the structure viewed along the *b* axis with the numbering scheme for Δ-$[Co(en)_3]_2(d\text{-tart})_3 \cdot 11.5H_2O$. Hydrogen bonds are indicated by broken lines. Italic symbols, F_2 and C_3, represent the modes of hydrogen bonds (see text).

angles in the complex and $tart^{2-}$ ions are listed in Tables SIV–SVI.[7] The least-squares planes of the $tart^{2-}$ ion are listed in Tables SVII–SIX.[7] The selected values for the distances and angles concerning hydrogen bonds are listed in Tables SX–SXII.[7]

Hydrogen-Bonding Modes. Each of the three crystals, I–III, contains two crystallographically independent $[Co(en)_3]^{3+}$ ions (Co1 and Co2) and three crystallographically independent $tart^{2-}$ (T1, T2, and T3) ions (Figures 1–3). All the complex ions in the three crystals have the $(lel)_3$ conformation. The average values of chemically equivalent bond distances and bond angles are in good agreement with the corresponding values reported previously.[8,9] The bond distances in the $tart^{2-}$ ions show small fluctuations, probably due to the disordered character. However, the four carbon atoms of all the $tart^{2-}$ ions lie almost in the same plane, and the $OCCOO^-$ part is also nearly planar. This conformation is common to most of the *d*-$tart^{2-}$ ions in crystal.[9,10]

The hydrogen bonds between the complex ions and the $tart^{2-}$ ions or the water molecules shown in Tables SX–SXII are classified into five categories (Figures 1–3): F_1, face-to-face hydrogen bonds between Λ-$[Co(en)_3]^{3+}$ and *d*-$tart^{2-}$ ions or between Δ-$[Co(en)_3]^{3+}$ and *l*-$tart^{2-}$ ions; F_2, face-to-face hydrogen bonds between Δ-$[Co(en)_3]^{3+}$ and *d*-$tart^{2-}$ ions or between Λ-$[Co(en)_3]^{3+}$ and *l*-$tart^{2-}$ ions; C_3, hydrogen bonds that are formed between the N–H bonds directed along the C_3 axis of $[Co(en)_3]^{3+}$ and the COO^- group of the $tart^{2-}$ ion; C_2, hydrogen bonds that are formed between the N–H bonds directed along the C_2 axis of $[Co(en)_3]^{3+}$ and the COO^- group of the $tart^{2-}$ ion; E_x, hydrogen bonds that do not belong to the preceding four categories.

In previous papers[9,11] hydrogen bonds of the F_1 type are reported to occur in a special local block. The hydrogen bonds of the F_2 type have not previously been reported. However, rather similar hydrogen bonds have been found recently in the combination of Δ-$[Co(sen)]^{3+}$ (sen = 5-methyl-5-(4-amino-2-azabutyl)-3,7-diazanonane-1,9-diamine) and *d*-$tart^{2-}$ ions.[12] Hydrogen bonds of the C_3 type have been also found in crystals of $[Ni(en)_3](CH_3COO)_2$[13] and $[Ni(en)_3]$ $(d,l\text{-tart})\cdot H_2O$.[1] Hydrogen bonds of the C_2 type can be found in all crystals that contain hydrogen bonds of the F_1 type.

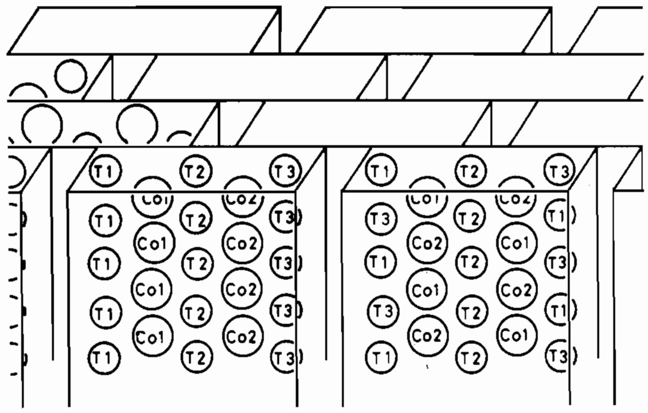

Figure 4. Schematic drawing of the crystal structures of the three salts. The complex ions are indicated as Co1 and Co2, and tartrate ions, as T1, T2, and T3. The arrangement of the ions in the right block corresponds to that in Figures 1 and 2, and that in the left block, to that in Figure 3.

Table V. Face-to-Face Ion-Pair Combinations for Crystals I–III

	Co1–T1	Co2–T2	Co2–T3
Δ,Λ-$[Co(en)_3]_2(d,l\text{-tart})_3 \cdot 10H_2O$	Λ–*d*	Λ–*l*	Δ–*d*
	Δ–*l*	Δ–*d*	Λ–*l*
Λ-$[Co(en)_3]_2(d\text{-tart})_3 \cdot 19H_2O$	Λ–*d*	Λ–*d*	Λ–*d*
Δ-$[Co(en)_3]_2(d\text{-tart})_3 \cdot 11.5H_2O$	Δ–*d*		Δ–*d*

Crystal Packing around the Tartrate Ions. A characteristic and common feature in the three crystal structures is that they are composed of piles of blocks, as shown schematically in Figure 4, where the complex and the $tart^{2-}$ ions are indicated as large and small circles, respectively. In each block, three crystallographically independent $tart^{2-}$ ions (T1, T2, and T3) and two crystallographically independent complex ions (Co1 and Co2) are arranged in the following order: $tart^{2-}$–complex–$tart^{2-}$–complex–$tart^{2-}$. This block corresponds to that in Figure 1–3; that is, the arrangment of ions is T1(or 3)–Co1(or 2)–T2–Co2(or 1)–T3(or 1) from left to right in the figures. When these blocks are piled three-dimensionally as in Figure 4, the structure is represented as in parts a, b, and c of Figure 5 for crystals I–III, respectively. These are depicted such that the structure in Figure 4 is viewed from the top to the bottom. In each structure, three $tart^{2-}$ ions (T1, T2, and T3) form various face-to-face combinations with two complex ions (Co1 and Co2). The face-to-face combination modes of these ions are summarized in Table V.

The $tart^{2-}$ ions in these crystals are classified into two groups according to their mode of packing with surrounding ions.

(a) T1 and T3. Inspection of Figures 1–3 reveals that T1 and T3 are packed in the same manner in each case; i.e., the positions of T1 and T3 are both the right and left borders of a block. At each position, the $tart^{2-}$ ion directs one of its carboxyl groups down the paper and another carboxyl group up the paper.

(b) T2. Each crystal shows the following common features concerning the packing mode of T2: (i) it is located at the middle of a block; (ii) its two carboxyl groups are directed parallel to the plane of the paper; (iii) it is surrounded by four complex ions.

Discussion

Since only the Λ–*d* and Δ–*l* combinations were found to produce face-to-face close contact in the crystals of Δ,Λ-$[Ni(en)_3](d,l\text{-tart})\cdot H_2O$, the same combinations were expected to lead to face-to-face close contact in the crystals of Δ,Λ-$[Co(en)_3]_2(d,l\text{-tart})_3 \cdot 10H_2O$ as well. However, crystal structure analyses reported here revealed that not only the Λ–*d* and Δ–*l* combinations but

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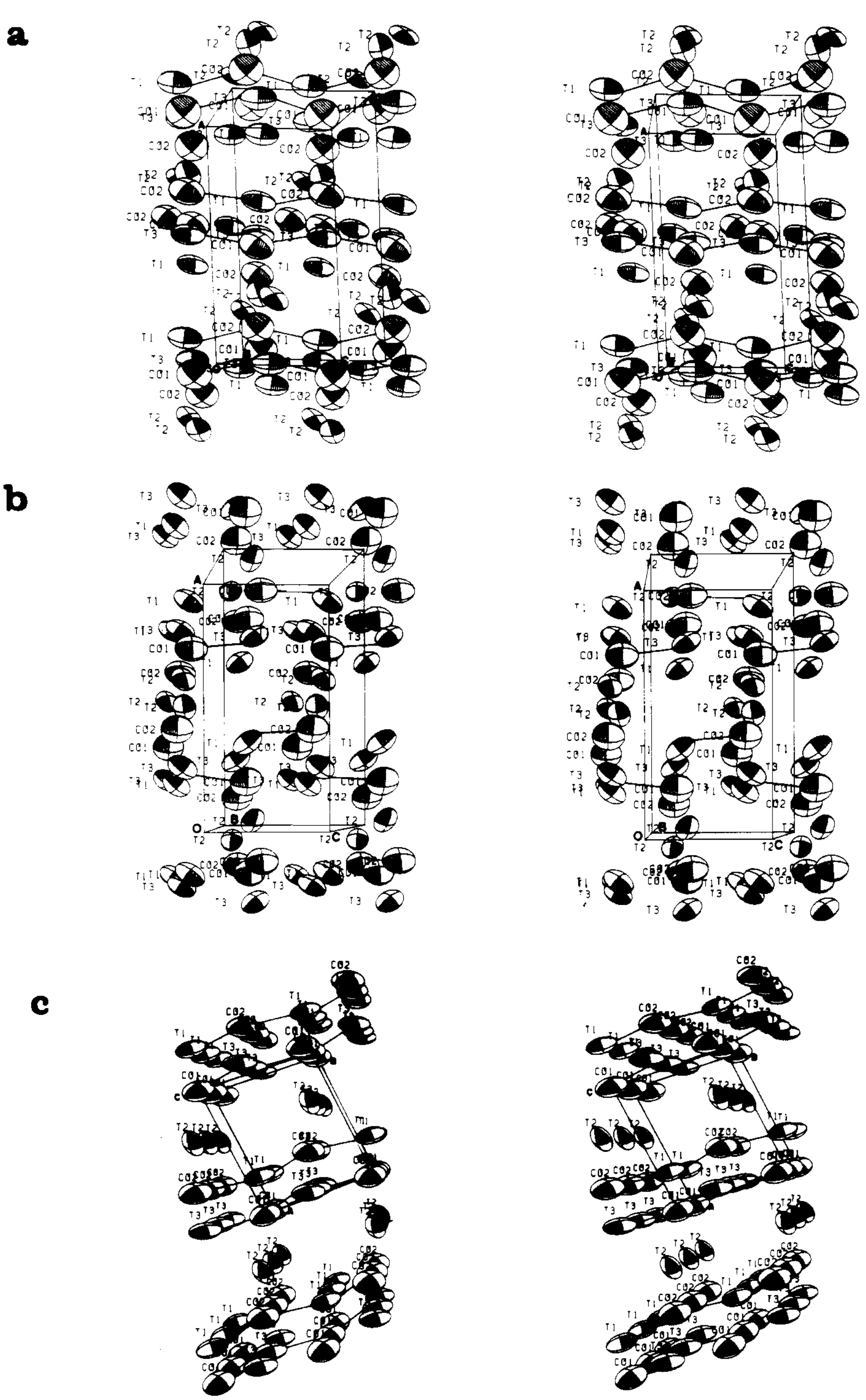

Figure 5. Stereoscopic views of the arrangement of the complex ions (Co1 and Co2) and tartrate ions (T1, T2, and T3) in crystal I (a), crystal II (b), and crystal III (c). Ellipsoids represent the complex and the tartrate ions. The C_3 axis of the complex ion corresponds to the shortest axis of the ellipsoid. An ellipsoid of tartrate ion is defined as follows: direction of the longest axis of the ellipsoid is along two carboxylate carbons. The shortest is perpendicular to the plane defined by four carbon atoms, and third axis is perpendicular to the other axes. Hydrogen bonds that connect the adjacent blocks are indicated by solid lines, and they are depicted in more detail in Figure 6.

also the Δ-*d* and Λ-*l* combinations lead to face-to-face close contact. This is not surprising when we recall that a face-to-face ion-pair structure in solution was already established for the unfavorable combination of ions (Δ-*d* or Λ-*l*) as well as the favorable combination (Λ-*d* or Δ-*l*).[14,15] Rather, it is surprising that such a face-to-face close contact mode of the unfavorable ion pair has not been found in the crystal so far. The situation should be considered in the following way. In thinking of the close contact mode of a specified ion pair in the crystal, one's attention should not be confined to the specified ion pair, since it holds its contact mode under the influence of all interactions exerted from the surrounding ions. In the favorable combination, the stability of the face-to-face contact mode is so great that the surrounding ions arrange themselves so as to keep the face-to-face close contact mode of the specified ion pair. In contrast, the contact mode of the unfavorable ion pair is not so stable as to maintain its face-to-face structure and its occurrence is dependent on the interactions exerted from the surrounding ions. Thus face-to-face close contact occurs in some cases but not in others, as follows.

(I) Comparison of the Packing Modes of T1 and T3 in the Three Crystals. T1 and T3 form face-to-face hydrogen-bonded ion pairs in each block of the three crystal structures (F_1 or F_2 mode in Figures 1–3). Each of these tart^{2-} ions (T1 and T3) in each block

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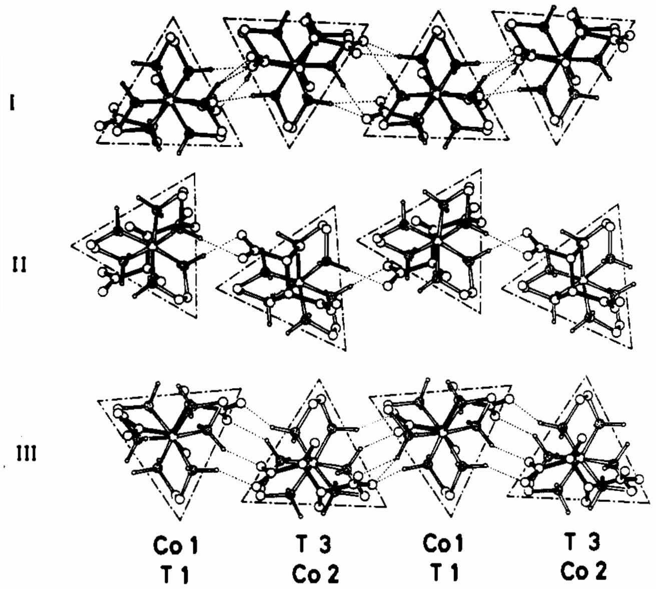

Figure 6. Drawing of part of the hydrogen bonding between ion pairs in adjacent blocks for three salts: Δ,Λ-$[Co(en)_3]_3(d,l\text{-tart})_3 \cdot 10H_2O$ (I), Λ-$[Co(en)_3]_2(d\text{-tart})_3 \cdot 19H_2O$ (II), and Δ-$[Co(en)_3]_2(d\text{-tart})_3 \cdot 11.5H_2O$ (III). Each complex ion is outlined as a regular triangle, and tartrate ions are indicated in black. Hydrogen bonds of the C_2 mode (see text) are represented by broken lines. Hydrogen atoms except for amino protons are eliminated for clarity.

is also linked to the complex ion in the adjacent block through hydrogen bonding of the C_2 mode using its carboxyl group (Figure 5).

The modes of hydrogen bonding between ion pairs in adjacent blocks in I–III are shown in more detail in Figure 6, where four face-to-face ion pairs (Co1 over T1), (T3 over Co2), (Co1 over T1), and (T3 over Co2), are connected to each other through hydrogen bonding (C_2 mode).

Viewed along the C_3 axis of the complex, the outline of a complex having three chelate rings is roughly depicted as a regular triangle (Figure 6). In the crystals of I(racemic) and III(Δ–d), the complex ions are linked together in such a way that their triangles are oriented in opposite directions. On the other hand, in the crystal of II(Λ–d), the triangles are arranged in such a way that their apexes are oriented in the same direction. Thus, it can be seen that the ion pairs are packed more densely in the former two crystals than in the latter. In fact, while the distance between the two complex ions in alternate blocks (the distance between the two Co1's, which is equal to twice the thickness of a block) is 12.067 Å (the *c* axis of I) and 12.145 Å (the *b* axis of III) in the former two cases, it is 12.849 Å (the *c* axis of II) in the latter case, which is definitely larger than those of the former two along this direction. The larger value in the latter case suggests that the ions are more loosely packed in II than in the former two cases (I and III).

As to the number of hydrogen bonds that connect the adjacent blocks, attention should be paid to the fact that the face-to-face ion pairs (T1 over Co1) and (Co2 over T3) in the adjacent blocks in the former two cases (I and III) are connected to each other through two sets of hydrogen bonds, T1···Co2 and Co1···T3 (C_2 mode in Tables SX and SXII). Thus, the two adjacent blocks can be considered as pasted tightly together by these two sets of hydrogen bonds. On the other hand, the two adjacent blocks in II(Λ–d) are connected by only one set of hydrogen bonds between Co1 and T3 or Co2 and T1 (C_2 mode in Table SXI).

Thus, considering the number of hydrogen bonds as well as the packing mode, the crystals of I(racemic) and III(Δ–d) are more favorably packed than the crystal of II(Λ–d), at least concerning the junction of T1, T3, and the complexions in the adjacent blocks.

(II) Comparison of the Packing Modes of T2 in the Three Crystals. In contrast to T1 and T3, T2 shows the expected packing mode. While face-to-face close contact occurs between the complex and $tart^{2-}$ (T2) ions in crystals I and II, both of which contain favorable combinations of ions, such as Λ–d and Δ–l, unfavorable face-to-face close contact of T2 is not found in III, which contains only the unfavorable combination Δ–d. Thus, the packing modes as a whole in I and II are quite different from that in III. It is worth noting that the packing modes in I and II are similar to that found in Δ,Λ-$[Ni(en)_3](d,l\text{-tart}) \cdot H_2O$.[1]

The tightness of the packing mode of T2 in these crystals can be estimated as follows. In Figures 1 and 2, $tart^{2-}$ ions (T2) and complex ions (Co1 and Co2) can be considered to form separate zigzag chains along the *b* axis. Thus, the zigzag chain of T2 can be considered to be sandwiched between the two zigzag chains of Co1 and Co2. Here the distance *d* between the two chains of complex ions can be regarded as a measure of the tightness of the packing of $tart^{2-}$ and complex ions in the *ab* plane in Figures 1 and 2. The value of *d* is 7.0 and 7.4 Å in crystals I and II, respectively. A similar kind of zigzag chains of T2, Co1, Co2 in crystal III can be seen in the *ac* plane in Figure 3. The distance between the complex ions that sandwich the chain of T2 is 10.0 Å, which is much larger than the corresponding values of the former two cases. Consequently, it can be stated that T2, Co1, and Co2 are more densely packed in I and II than in III.

Conclusion

This study reconfirms that face-to-face close contact between the complex and $tart^{2-}$ ions always occurs in the crystals containing favorable combinations of ions, Λ–d and Δ–l. In addition, it was newly found that face-to-face close contact occurs even for unfavorable combinations of ions, Δ-d and Λ-l, depending upon the interactions from surrounding ions.

Comparison of the packing modes in the three crystals leads to the following conclusion. The crystal packing of II is tight around T2 but loose around T1 and T3. The reverse situation is seen for crystal III, which shows loose packing around T2 and tight packing around T1 and T3. In contrast, crystal I shows tight packing for all T's, T1, T2, and T3. Consequently, crystal I is concluded to be the most energetically stable among the three crystals. This conclusion is in good agreement with the fact that crystal I is far less soluble than II and III.

Supplementary Material Available: Projections of the crystal structure of I–III along the *b*, *b*, and *c* axes, respectively (Figures S1–S3), listings of derived hydrogen coordinates, bond distances and angles, least-squares planes of the $tart^{2-}$ ion, hydrogen-bond distances and angles, and thermal parameters for I–III (Tables SI–SXII) (23 pages); listings of observed and calculated structure factor amplitudes (Tables SXVI–SXVIII) (28 pages). Ordering information is given on any current masthead page.