

**[(*S*)-1-Carbamoylethyl]bis(dimethylglyoximato- $\kappa^2N,N'$ )[(*S*)-1-phenylethylamine]cobalt(III) and bis(dimethylglyoximato- $\kappa^2N,N'$ )[(*R*)-1-(*N*-methylcarbamoyl)ethyl][(*R*)-1-phenylethylamine]cobalt(III) monohydrate**

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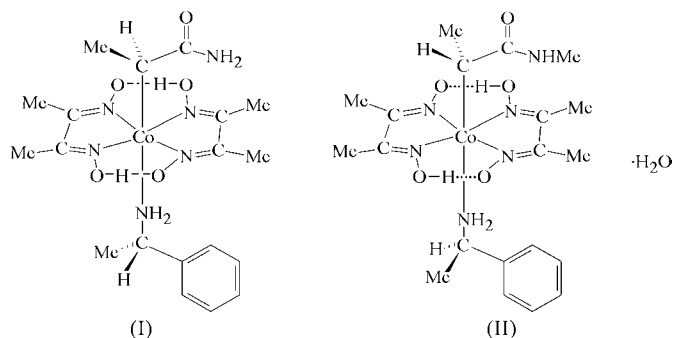
The title complexes, [Co(C<sub>3</sub>H<sub>6</sub>NO)(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>11</sub>N)] and [Co(C<sub>4</sub>H<sub>8</sub>NO)(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>11</sub>N)]·H<sub>2</sub>O, were resolved from [(*RS*)-1-carbamoylethyl]bis(dimethylglyoximato)-[(*S*)-1-phenylethylamine]cobalt(III) and bis(dimethylglyoximato)[(*RS*)-1-(*N*-methylcarbamoyl)ethyl][(*R*)-1-phenylethylamine]cobalt(III), respectively, and their crystal structures were determined in order to reveal the absolute configuration of the major enantiomer produced in the photoisomerization of each series of 2-carbamoylethyl and 2-(*N*-methylcarbamoyl)ethyl cobaloxime complexes.

**Comment**

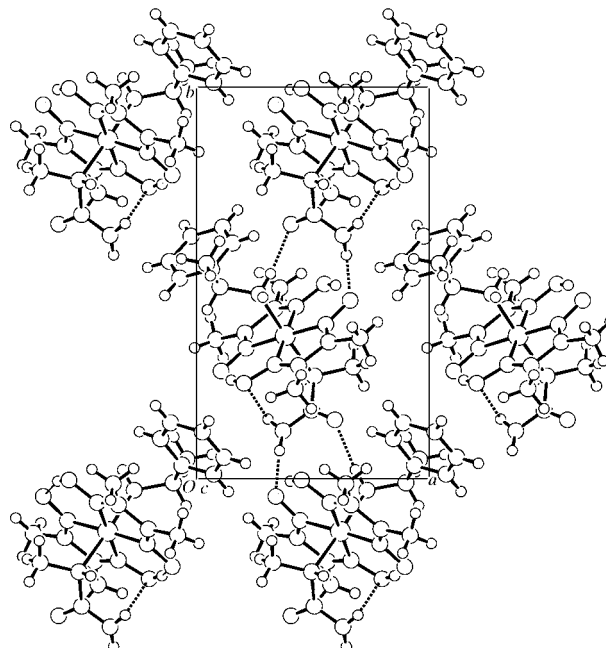
Solid-state specific and monodirectional photoisomerization of 2-cyanoethyl, 2-methoxycarbonylethyl, 2-carbamoylethyl, 2-(*N*-methylcarbamoyl)ethyl and 3-substituted-propyl cobaloximes have been reported previously (Ohgo & Takeuchi, 1985; Kurashima *et al.*, 1995; Ohgo *et al.*, 1994, 1996, 2000, 2001). Moreover, asymmetric induction was found to occur in the  $\beta \rightarrow \alpha$  photoisomerization of various 2-substituted-ethyl cobaloximes having chiral axial ligands as the chiral handle for forming the chiral lattice (Ohgo *et al.*, 1994, 1996, 1997, 2000). However, the absolute configuration of the alkyl moiety of each chiral product has not yet been determined in the cases of the series of 2-carbamoylethyl and 2-(*N*-methylcarbamoyl)ethyl cobaloximes. The crystal structure analyses of the title complexes were undertaken to reveal the configurational correlation of asymmetric photoisomerization.

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The crystal structure of the title 1-carbamoylethyl complex, (I), viewed along the *c* axis, and a stereoview of the crystal structure of the 1-(*N*-methylcarbamoyl)ethyl complex, (II), are shown in Figs. 1 and 2, respectively. The molecular structures of (I) and (II) are shown in Figs. 3 and 4, respectively. The absolute configuration (*S*) of the 1-carbamoylethyl group in (I) was set by reference to the known chirality of the axial base, (*S*)-1-phenylethylamine. Similarly, the absolute configuration (*R*) of the 1-(*N*-methylcarbamoyl)ethyl group in (II) was set by reference to that of the coordinated (*R*)-1-phenylethylamine. Selected bond distances and angles are given in Tables 1 and 3, respectively. The hydrogen bonds in (I) and (II) are given in Tables 2 and 4, respectively.



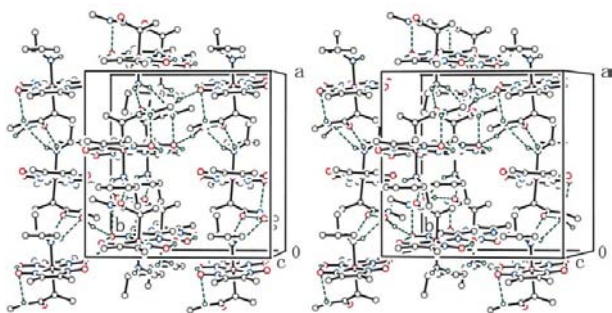
The molecular structures of (I) and (II) essentially maintain similar structural features except for their configurations. Each C<sub>alkyl</sub>—Co—N<sub>amine</sub> moiety is almost linear: the C9—Co—N5 and C9—Co—N6 angles in (I) and (II) are 177.3 (1) and 177.8 (2)°, respectively. Both the carbamoyl group and the phenylethyl group of the axial base of each complex are located on the same side, namely the O2/O3 side in (I) and the O1/O4 side in (II); the C12—N5—C9—C10 and C13—N6—



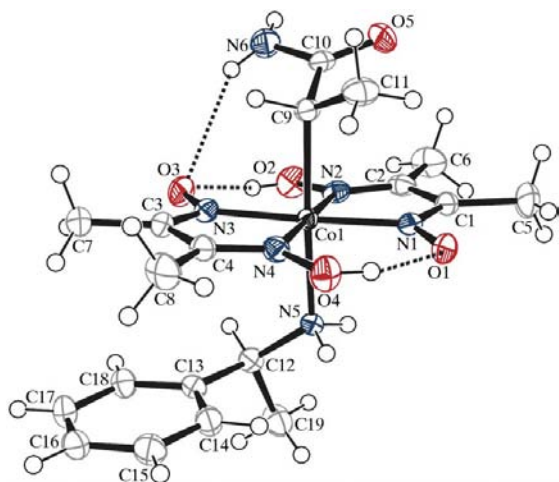
**Figure 1**  
Projection of the crystal structure of complex (I), viewed along the *c* axis. Dotted lines indicate the hydrogen bonds.

C9—C10 torsion angles in (I) and (II) are  $-85.3(2)$  and  $70.7(6)^\circ$ , respectively. The N—H bond of each carbamoyl group is directed to one of the O atoms on the planar ligands to form an intramolecular hydrogen bond [N6—H6D $\cdots$ O3 in (I) and N5—H5 $\cdots$ O4 in (II)]. The aromatic ring lies parallel with the Co—glyoxime plane, Co/C3/C4/N3/N4, and the dihedral angles between this plane and the aromatic rings, C13—C18 in (I) and C14—C19 in (II), are  $8.8(2)$  and  $12.7(1)^\circ$ , respectively.

Adjacent molecules in the structure of (I) are connected by intermolecular N5—H5B $\cdots$ O5<sup>i</sup> and N6—H6E $\cdots$ O1<sup>ii</sup> hydrogen bonds [symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, -z$ ; (ii)  $1 - x, y - \frac{1}{2}, -z$ ], forming chains along the *b* axis. In the structure of (II), adjacent molecules are linked into a three-dimensional network by intermolecular hydrogen bonds involving the solvent water molecule, the coordinated amine group and the amide group of the 1-(*N*-methylcarbamoyl)ethyl moiety. Thus, the molecules are interconnected, forming chains along the *a* axis through intermolecular N6—



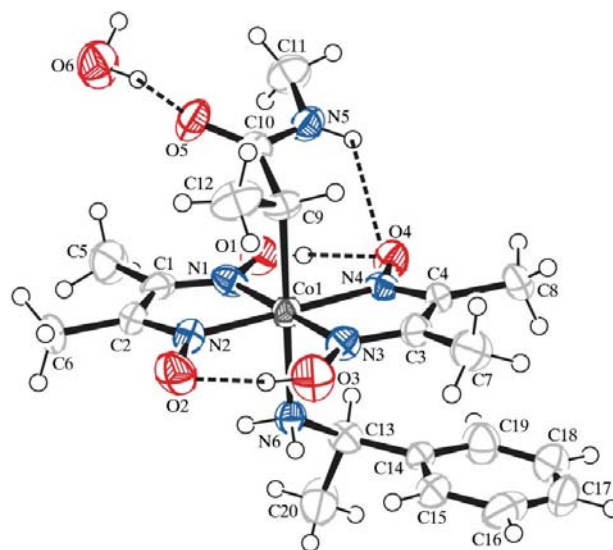
**Figure 2**  
A stereoview of the crystal structure of complex (II). Dotted lines show the hydrogen bonds. H atoms bonded to C atoms have been omitted for clarity.



**Figure 3**  
The molecular structure of complex (I) with the atomic numbering. Dotted lines indicate the hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level.

H6E $\cdots$ O5<sup>ii</sup> hydrogen bonds [symmetry code: (ii)  $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ ]. Each chain so formed is connected to four neighbouring chains by bridging water molecules *via* three intermolecular hydrogen bonds, *viz.* N6—H6D $\cdots$ O6<sup>ii</sup>, O6—H6G $\cdots$ O5 and O6—H6F $\cdots$ O4<sup>i</sup> [symmetry code: (i)  $\frac{1}{2} - x, -y, \frac{1}{2} + z$ ], to form a three-dimensional hydrogen-bond network.

The axial base of (II) was displaced by methyl-diphenylphosphine to afford bis(dimethylglyoximate)[(*R*)-1-(*N*-methylcarbamoyl)ethyl](methyl-diphenylphosphine)cobalt(III) [optical rotation  $[\alpha]_{589} = +28.6$ ,  $[\alpha]_{578} = +23.7$  and  $[\alpha]_{546} = +2.0$  ( $c = 0.101$ , CHCl<sub>3</sub>)], which was analyzed by high-performance liquid chromatography (HPLC) using a chiral column. The powdered sample of bis(dimethylglyoximate)-[2-(*N*-methylcarbamoyl)ethyl][methyl (*S*)-phenylalaninate]-cobalt(III), (III) (Ohgo *et al.*, 1996, 2000), was irradiated with a solar simulator (flux density 100 mW cm<sup>-2</sup>) to give a diastereomeric mixture of bis(dimethylglyoximate)[1-(*N*-methylcarbamoyl)ethyl][methyl(*S*)-phenylalaninate]cobalt(III), which was also analyzed by HPLC after displacement of the axial ligand with methyl-diphenylphosphine. From a comparison of the results of the HPLC analysis of these samples, the absolute configuration of the major enantiomer produced by photoisomerization of complex (III) was determined to be *S*. On the other hand, the axial base of (I) was displaced by dimethylphenylphosphine to afford [(*S*)-1-carbamoyl ethyl]bis(dimethylglyoximate)(dimethylphenylphosphine)cobalt(III), (IV) [optical rotation  $[\alpha]_{589} = -47.9$ ,  $[\alpha]_{578} = -47.9$  and  $[\alpha]_{546} = -46.2$  (CHCl<sub>3</sub>)]. The configuration of the major enantiomer produced by irradiation of the powdered crystals of a series of 2-carbamoyl ethyl cobaloximes was also revealed from a comparison of the optical rotation of complex (IV) with that of the photoisomerization products treated with dimethylphenylphosphine.



**Figure 4**  
The molecular structure of complex (II), with the atomic numbering. Dashed lines indicate the hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Complexes (I) and (II) were prepared according to the literature method of Ohgo *et al.* (1996). [(*RS*)-1-carbamoylethyl]bis(dimethylglyoximate)[(*S*)-1-phenylethylamine]cobalt(III) was recrystallized five times from dichloromethane–hexane (1:1) to afford yellow crystals of complex (I), with maximum optical rotation [ $\alpha$ ]<sub>589</sub> = +27.6, [ $\alpha$ ]<sub>578</sub> = +41.4 and [ $\alpha$ ]<sub>546</sub> = +100.5 ( $c$  = 0.102, CHCl<sub>3</sub>). Analysis found: C 47.1, H 6.4, N 17.2%; calculated for C<sub>19</sub>H<sub>31</sub>CoN<sub>6</sub>O<sub>5</sub>: C 47.3, H 6.5, N 17.4%. Bis(dimethylglyoximate)[(*RS*)-1-(*N*-methylcarbamoyl)ethyl]-[(*R*)-1-phenylethylamine]cobalt(III) was recrystallized six times from a benzene–hexane (1:1) and finally from a mixture of benzene [including 1% (*R*)-phenylethylamine] and hexane (5:1) to afford dark-red crystals of complex (II) with maximum optical rotation [ $\alpha$ ]<sub>589</sub> = –60.4, [ $\alpha$ ]<sub>578</sub> = –82.5 and [ $\alpha$ ]<sub>546</sub> = –158.2 ( $c$  = 0.104, CHCl<sub>3</sub>). Analysis found: C 46.9, H 6.8, N 16.3%; calculated for C<sub>20</sub>H<sub>35</sub>CoN<sub>6</sub>O<sub>6</sub>: C 46.7, H 6.9, N 16.3%.

Compound (I)

Crystal data

[Co(C<sub>3</sub>H<sub>6</sub>NO)(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>·(C<sub>8</sub>H<sub>11</sub>N)]  
*M<sub>r</sub>* = 482.43  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>  
*a* = 8.743 (2) Å  
*b* = 14.696 (3) Å  
*c* = 8.565 (3) Å  
 $\beta$  = 93.29 (2)°  
*V* = 1098.7 (5) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.458 Mg m<sup>–3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 12.6–14.9°  
 $\mu$  = 0.82 mm<sup>–1</sup>  
*T* = 223 K  
 Needle, yellow  
 0.23 × 0.18 × 0.17 mm

Data collection

Rigaku AFC-7R diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
*T*<sub>min</sub> = 0.789, *T*<sub>max</sub> = 0.869  
 3200 measured reflections  
 2624 independent reflections  
 2404 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.027  
 $\theta_{\max}$  = 27.5°  
*h* = –6 → 11  
*k* = 0 → 19  
*l* = –11 → 11  
 3 standard reflections every 100 reflections  
 intensity decay: 0.7%

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.025  
*wR*(*F*<sup>2</sup>) = 0.066  
*S* = 1.21  
 2624 reflections  
 299 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Absolute structure: Flack (1983), 2 Friedel pairs  
 Flack parameter: –0.004 (14)

Table 1

Selected geometric parameters (Å, °) for (I).

Co1–N4	1.879 (2)	Co1–C9	2.092 (3)
Co1–N2	1.888 (2)	O5–C10	1.236 (3)
Co1–N1	1.890 (2)	N6–C10	1.350 (4)
Co1–N3	1.892 (2)	C9–C10	1.497 (4)
Co1–N5	2.077 (2)	C9–C11	1.529 (4)
N5–Co1–C9	177.3 (1)	O5–C10–N6	121.1 (3)
C10–C9–C11	111.2 (2)	O5–C10–C9	122.2 (3)
C10–C9–Co1	110.8 (2)	N6–C10–C9	116.6 (3)
C11–C9–Co1	114.7 (2)		

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O2–H2...O3	0.83	1.73	2.515 (3)	158
O4–H4...O1	0.83	1.71	2.506 (3)	160
N5–H5B...O5 <sup>i</sup>	0.91	2.12	2.925 (3)	147
N6–H6D...O3	0.83 (5)	2.53 (5)	3.249 (4)	145 (4)
N6–H6E...O1 <sup>ii</sup>	0.92 (5)	2.10 (5)	3.021 (4)	176 (4)

Symmetry codes: (i) –*x* + 1, *y* + ½, –*z*; (ii) –*x* + 1, *y* – ½, –*z*.

Compound (II)

Crystal data

[Co(C<sub>4</sub>H<sub>8</sub>NO)(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>·(C<sub>8</sub>H<sub>11</sub>N)]·H<sub>2</sub>O  
*M<sub>r</sub>* = 514.47  
 Orthorhombic, *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub>  
*a* = 14.1206 (19) Å  
*b* = 14.169 (2) Å  
*c* = 12.372 (2) Å  
*V* = 2475.3 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.380 Mg m<sup>–3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 12.8–14.7°  
 $\mu$  = 0.74 mm<sup>–1</sup>  
*T* = 293 K  
 Needle, red  
 0.25 × 0.15 × 0.12 mm

Data collection

Rigaku AFC-7R diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
*T*<sub>min</sub> = 0.838, *T*<sub>max</sub> = 0.917  
 4662 measured reflections  
 3581 independent reflections  
 1749 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.039  
 $\theta_{\max}$  = 27.5°  
*h* = –10 → 18  
*k* = 0 → 18  
*l* = –9 → 16  
 3 standard reflections every 100 reflections  
 intensity decay: –0.8%

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.105  
*S* = 0.98  
 3581 reflections  
 317 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.029P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.80 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Absolute structure: Flack (1983), 387 Friedel pairs  
 Flack parameter: 0.02 (3)

Table 3

Selected geometric parameters (Å, °) for (II).

Co1–N3	1.868 (5)	O5–C10	1.229 (7)
Co1–N1	1.889 (5)	N5–C10	1.342 (8)
Co1–N2	1.890 (5)	N5–C11	1.470 (8)
Co1–N4	1.894 (5)	C9–C10	1.504 (8)
Co1–N6	2.070 (4)	C9–C12	1.534 (8)
Co1–C9	2.080 (5)		
N6–Co1–C9	177.8 (2)	C12–C9–Co1	115.0 (4)
C10–N5–C11	122.2 (5)	O5–C10–N5	120.9 (6)
C10–C9–C12	110.8 (5)	O5–C10–C9	123.0 (7)
C10–C9–Co1	112.1 (4)	N5–C10–C9	116.1 (6)

Water H atoms were located in difference maps; O–H distances were constrained to 0.95 Å and *U*<sub>iso</sub>(H) values were set at 1.2*U*<sub>eq</sub>(O). All other H atoms were refined using a riding model, with C–H distances of 0.96 Å for primary, 0.97 Å for secondary and 0.93 Å for aromatic H atoms, and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) (1.5 for methyl groups). The absolute structures were set by reference to the known chirality of the enantiopure amine coordinated in each complex and the Flack (1983) parameters are in agreement with each expected configuration.

**Table 4**

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O4	0.82	1.75	2.536 (6)	159
O3—H3 $\cdots$ O2	0.82	1.71	2.499 (6)	162
O6—H6F $\cdots$ O4 <sup>i</sup>	0.97 (3)	1.96 (5)	2.787 (6)	143 (6)
O6—H6G $\cdots$ O5	0.96 (3)	1.89 (4)	2.813 (7)	162 (7)
N5—H5 $\cdots$ O4	0.86	2.49	3.030 (7)	122
N6—H6D $\cdots$ O6 <sup>ii</sup>	0.90	2.36	3.108 (7)	141
N6—H6E $\cdots$ O5 <sup>ii</sup>	0.90	2.39	3.163 (6)	143

Symmetry codes: (i)  $-x + \frac{1}{2}, -y, z + \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1998); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *MULTAN88* (Debaerdemaeker *et al.*, 1988) for (I); *SIR92* (Altomare *et al.*, 1993) for (II). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SV* (Nemoto & Ohashi, 1993) and *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1367). Services for accessing these data are described at the back of the journal.

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