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# Cadmium(II) thio- and selenocyanate complexes of 3,3′-bis(1,2,4-triazol-4-yl)-1,1′-biadamantane, a ligand designed with an 'extended nanodiamond' aliphatic platform

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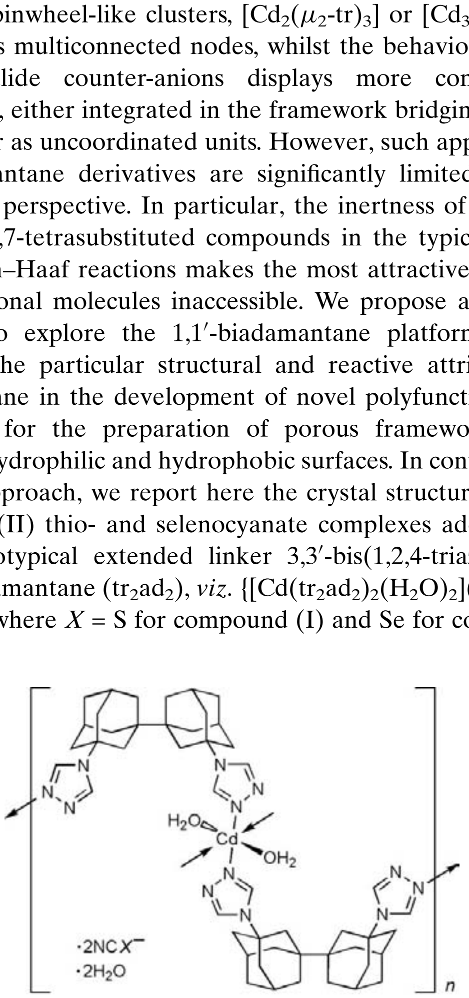
In the structures of the Cd$^{II}$ pseudohalide coordination polymer poly[[diaquabis[$\mu_2$-3,3′-bis(1,2,4-triazol-4-yl)-1,1′-biadamantane-$\kappa^2N^1$:$N^{1'}$]cadmium(II)] dithiocyanate dihydrate], {[Cd($C_{24}H_{32}N_6$)$_2$($H_2O$)$_2$](NCS)$_2$·2$H_2O$}$_n$, (I), and the isomorphous selenocyanate analogue, {[Cd($C_{24}H_{32}N_6$)$_2$($H_2O$)$_2$](NCSe)$_2$·2$H_2O$}$_n$, (II), the Cd$^{II}$ cations occupy inversion centres and have octahedral Cd$N_4O_2$ environments, completed by four N atoms of the organic ligands [Cd—N = 2.316 (2) and 2.361 (2) Å for (I), and 2.313 (3) and 2.372 (3) Å for (II)] and two *trans*-coordinated aqua ligands [Cd—O = 2.3189 (15) Å for (I) and 2.323 (2) Å for (II)]. In each compound, the ligand displays a bidentate $N^1$:$N^{1'}$-bridging mode, connecting the metal centres at a distance of 14.66 Å into two-dimensional nets of (4,4)-topology, while the uncoordinated thio(seleno)cyanate anions reside inside the net cavities. Hydrogen bonding between the water molecules, anions and 1,2,4-triazole N atoms supports the tight packing, with an interlayer distance of 6.09 Å.

## Comment

Cage hydrocarbons, such as adamantane, diamantane and related nanodiamond species, provide unique molecular scaffolds for a wide variety of accurate and geometrically elegant ligands supporting the structures of robust and thermally stable metal–organic frameworks (MOFs). Most efforts in this area have been focused on a single adamantane-supported platform containing two or four carboxylate functions and their further multi-connector roles in the MOFs of adamantane-1,3-dicarboxylate with Zn$^{II}$ (Nielsen *et al.*, 2008) or Eu$^{III}$ (Millange *et al.*, 2004), and adamantane-1,3,5,7-tetracarboxylate with Cu$^{II}$ (Chen *et al.*, 2000), Ni$^{II}$ and Zn$^{II}$ (Kim *et al.*, 2001) or Cd$^{II}$ (Rosi *et al.*, 2005). Even more versatile possibilities may be anticipated for heteroaryl-functionalized adamantanes. Mono- and bitopic 1,2,4-triazole (tr) derivatives built up on the adamantane backbone have offered an interesting perspective in the design of Cd$^{II}$, Cu$^{II}$ (Senchyk *et al.*, 2009) and Mo$^{VI}$ coordination polymers (Lysenko *et al.*, 2010). The remarkable binding ability of the tr heterocycle affords cationic pinwheel-like clusters, [Cd$_2$($\mu_2$-tr)$_3$] or [Cd$_3$($\mu_2$-tr)$_6$], serving as multiconnected nodes, whilst the behaviour of the pseudohalide counter-anions displays more complicated character, either integrated in the framework bridging the co-ligands or as uncoordinated units. However, such applications of adamantane derivatives are significantly limited from a synthetic perspective. In particular, the inertness of 1,3,5-tri- and 1,3,5,7-tetrasubstituted compounds in the typical Ritter and Koch–Haaf reactions makes the most attractive types of polyfuntional molecules inaccessible. We propose a strategy aiming to explore the 1,1′-biadamantane platform, which marries the particular structural and reactive attributes of adamantane in the development of novel polyfunctionalized modules for the preparation of porous frameworks with distinct hydrophilic and hydrophobic surfaces. In continuation of this approach, we report here the crystal structures of the cadmium(II) thio- and selenocyanate complexes adopted by the prototypical extended linker 3,3′-bis(1,2,4-triazol-4-yl)-1,1′-biadamantane (tr$_2$ad$_2$), *viz.* {[Cd(tr$_2$ad$_2$)$_2$($H_2O$)$_2$](NC$X$)$_2$·2$H_2O$}$_n$, where $X$ = S for compound (I) and Se for compound (II).



(I) $X$ = S
(II) $X$ = Se

Compounds (I) and (II) adopt an isomorphous two-dimensional polymeric motif which includes extended hydrogen bonding. The asymmetric units of the unit cells contain a Cd$^{II}$ cation, a thio(seleno)cyanate anion, a coordinated tr$_2$ad$_2$ ligand, and one coordinated and one solvent water molecule. The Cd$^{II}$ cations lie on inversion centres and exhibit octahedral environments, involving four N(tr) atoms in the equatorial plane [Cd—N = 2.316 (2) and 2.361 (2) Å for (I), and 2.313 (3) and 2.372 (3) Å for (II)] and two aqua molecules in the *trans*-axial positions [Cd—O = 2.3189 (15) Å for (I) and 2.323 (2) Å for (II)] (Fig. 1). A comparable set of bond lengths in an $N_4O_2$ environment was also observed for [Cd$_2$($L$)$_4$($H_2O$)$_4$](Cl$O_4$)$_4$·4$H_2O$, where $L$ is di-4-pyridylamine (Krishnan *et al.*, 2007). The ligands adopt an $N^1$:$N^{1'}$-bridging role between two adjacent Cd$^{II}$ cations in two directions [related by the symmetry operations ($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$) and

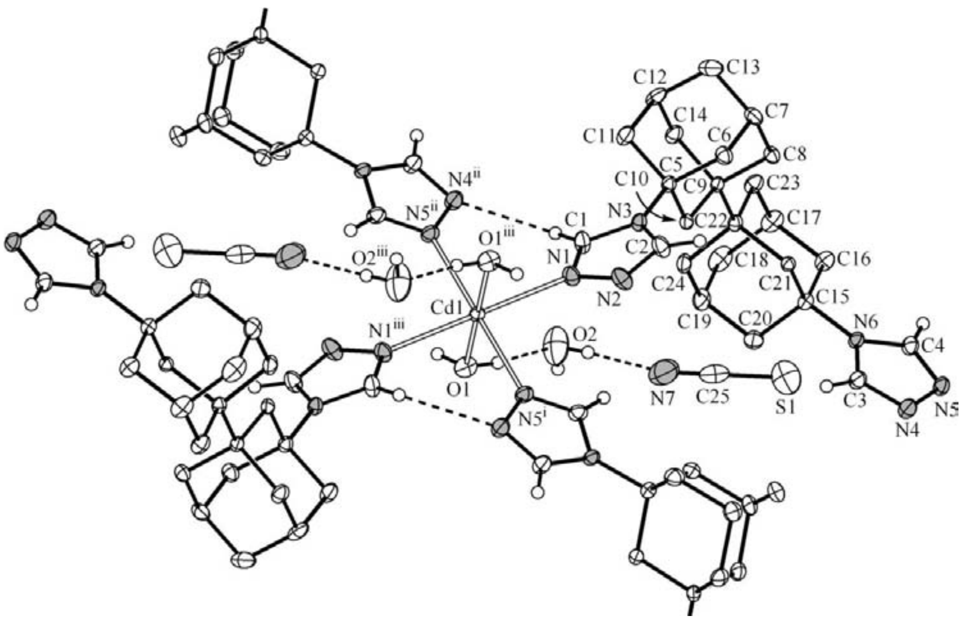


**Figure 1**
The structure of (I), showing the atom-labelling scheme [the structure of (II) is isomorphous]. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii. Aliphatic H atoms have been omitted for clarity and dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; (ii) $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $-x, 1 - y, -z$.]

$(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$] at a distance of 14.66 Å, giving a square net (Fig. 2). Similar $M^{II}(H_2O)_2(ligand)_2$ square-grid motifs have recently been reported for Cd and Cu complexes with 4,4′-bi-1,2,4-triazole (Huang *et al.*, 2008; Govor *et al.*, 2010), while in the case of the flexible bitriazole linker 1,2-bis(4*H*-1,2,4-triazol-4-yl)ethane, an alternative kind of polymorphic form supported by double bridging was also observed (Yi *et al.*, 2005).

With relatively free rotation around the single C—C bond linking two adamantane cores, the ligand displays an angular pseudo-*gauche* conformation and the corresponding dihedral angles defined by the three virtual bond vectors N3—C9, C9—C22 and C22—N6 ('tr–ad–ad–tr torsion') have approximate values of 72–73°. Thus, within the biadamantane core, the C8—C9—C22—C23 torsion angle is −72.3 (3)° in (I) and −73.6 (4)° in (II). Such a conformation gives rise to extended undulating $(Cd\text{-}tr_2ad_2)_n$ chains running along the crystallographic (211) and $(2\bar{1}\bar{1})$ axes. In the $[Cd(tr_2ad_2)_2(H_2O)_2]_n$ layer, two opposing biadamantane linkers of each $Cd_4(tr_2ad_2)_4$ square are directed towards one another and stacked parallel [the shortest distance is C14···C23$^{iv}$ of 3.835 (4) Å in (I); symmetry code: (iv) $-x, -y, -z$], causing significant geometric distortion of the net meshes (Fig. 2). In this way, the aliphatic portions of the ligands fill the centres of each $Cd_4(tr_2ad_2)_4$ square and generate two hydrophobic pores of *ca* 3.0 Å diameter. The ad–ad moieties are complementary in shape and additionally they mediate the hydrophobic interactions between neighbouring $[Cd(tr_2ad_2)_2(H_2O)_2]_n$ layers, resulting in their being arranged in a mutually parallel mode. The hydrophobic channels aligned along the *a* axis are occupied by $NCS^-$ (or $NCSe^-$) anions, which, in spite of their high nucleophilicity and affinity towards the Lewis soft $Cd^{II}$ centres, are left uncoordinated. This is the first example of uncoordinated behaviour of $NCSe^-$ in complexes with nonchelating ligands.

The $Cd(tr)_4(H_2O)_2$ moieties, as a distinct hydrophilic part of the networks, are especially beneficial for mediating different kinds of hydrogen-bonding interactions (Fig. 3). The anions are involved in hydrogen-bond interactions with coordinated

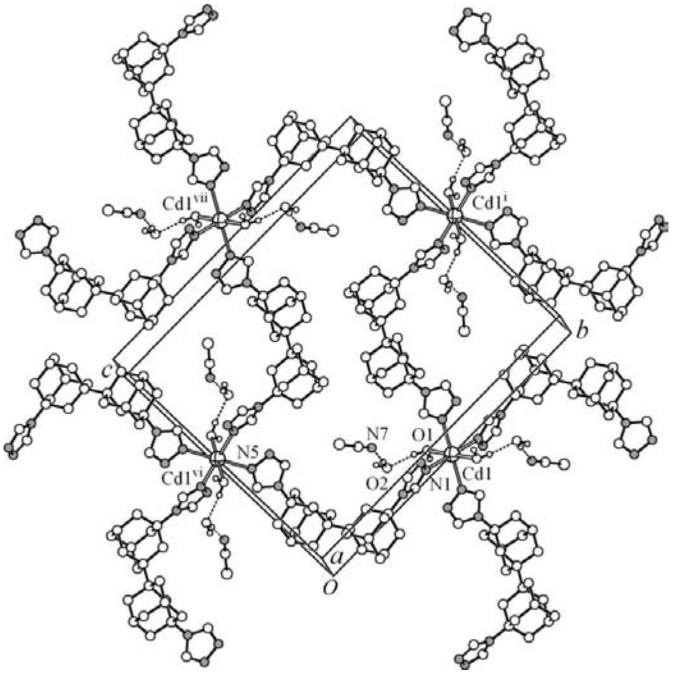


**Figure 2**
The two-dimensional network in the structure of (I) [the structure of (II) is isomorphous], supported by connecting $Cd^{II}$ ions with the extended $tr_2ad_2$ ligands. Aliphatic H atoms have been omitted and dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; (vi) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (vii) $2 + x, y, 1 + z$.]

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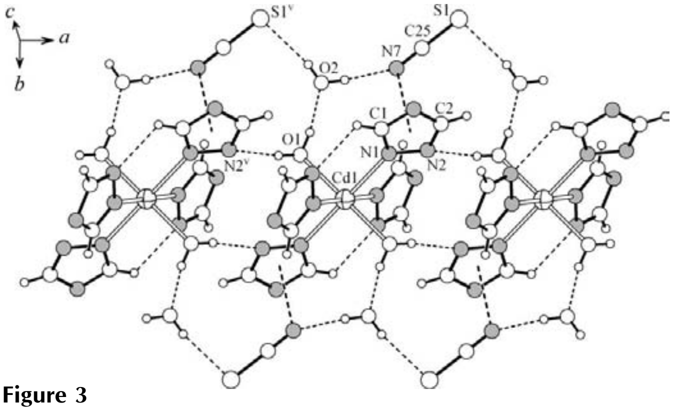

**Figure 3**
The interconnection of metal–organic layers along the *a* axis in the structure of (I), supported by multiple O—H···O, O—H···N, O—H···S and C—H···N hydrogen bonds and weak $\pi$–anion stacking between N ($NCS^-$ anion) and the triazole heterocycle. Dashed lines indicate hydrogen bonds and $\pi$–anion interactions. [Symmetry code: (v) $-1 + x$, $y$, $z$.]

and uncoordinated water molecules, yielding interconnection of the metal–organic layers into three-dimensional coordination and hydrogen-bonded frameworks. Thus, each aqua ligand behaves as a double hydrogen-bond donor, to the solvent water molecule and to atom N2 of a neighbouring layer (see Tables 1 and 2 for details). The solvent water molecules located in the interlayer region are further bound to atoms N7 and S1 of the pseudohalide anions. These interactions are accompanied by a weak anion–$\pi$ contact between the counter-anion and the $\pi$-deficient tr heterocycle [N7···*Cg*(tr) = 3.294 (4) Å for (I) and 3.285 (6) Å for (II); *Cg*(tr) is the centroid of the tr ring], with values similar to that observed in the Mn(NCS)$_2$ complex with 4,4′-bi-1,2,4-triazole (Zilverentant *et al.*, 1998). The interplay between the noncovalent interactions causes a substantial decrease in the interlayer distance (6.095 Å), thus forming the tight packing motifs.

In conclusion, our results demonstrate the potential of the novel organic ligand 3,3′-bis(1,2,4-triazol-4-yl)-1,1′-biadamantane (tr$_2$ad$_2$), which possesses attractive features such as rigidity, substantial size, thermal stability and special triazole functionality, in the construction of MOFs. The extra-large aliphatic spacers are involved in hydrophobic interactions that are a determinative attribute, giving rise to bulk pillars in the structure. Further functionalization of the 1,1′-biadamantane scaffold promises the expansion of abilities for designing stiff and porous coordination polymers with distinct hydrophobic and hydrophilic surfaces.

## Experimental

For the preparation of 3,3′-bis(1,2,4-triazol-4-yl)-1,1′-biadamantane (tr$_2$ad$_2$), a mixture of 3,3′-diamino-1,1′-biadamantane (0.800 g, 2.66 mmol), *N*,*N*-dimethylformamide azine (1.39 g, 9.77 mmol) and TsOH monohydrate (0.120 g, 0.697 mmol) in *o*-xylene (8 ml) was heated under reflux for 24 h. The reaction mixture was cooled to room temperature and the product was isolated by filtration and dried (yield 0.500 g, 46%). Complexes (I) and (II) were prepared in a similar way using a hydrothermal technique. Cd(NCS)$_2$ (9.9 mg, 0.043 mmol), tr$_2$ad$_2$ (10.0 mg, 0.025 mmol) and water (5 ml) were added to a Teflon vessel, placed in a steel bomb and heated to 443 K for 24 h. The mixture was cooled slowly to room temperature over a period of 48 h to afford colourless crystals of (I) together with a pale-yellow powder (yield 8.0 mg, 58%). The crystals were separated by repeated slurrying of the product in water followed by careful decantation. In a similar way, colourless crystals of complex (II) were prepared in 33% yield starting from Cd(NCSe)$_2$ (8.1 mg, 0.025 mmol) and tr$_2$ad$_2$ (10.0 mg, 0.025 mmol) in an ethanol–water solution (1:1 *v*/*v*).

### Compound (I)

*Crystal data*

| | |
|---|---|
| $[Cd(C_{24}H_{32}N_6)_2(H_2O)_2](NCS)_2\cdot 2H_2O$ | $\beta = 99.242\ (2)^\circ$ |
| $M_r = 1109.74$ | $V = 2534.3\ (3)$ Å$^3$ |
| Monoclinic, $P2_1/c$ | $Z = 2$ |
| $a = 6.8689\ (4)$ Å | Mo $K\alpha$ radiation |
| $b = 20.3896\ (12)$ Å | $\mu = 0.57$ mm$^{-1}$ |
| $c = 18.3330\ (11)$ Å | $T = 213$ K |
| | 0.22 × 0.20 × 0.04 mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII area-detector diffractometer | 13522 measured reflections |
| Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 2003) | 5535 independent reflections |
| $T_{min} = 0.884$, $T_{max} = 0.977$ | 4109 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.037$ |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | 4 restraints |
| $wR(F^2) = 0.098$ | H-atom parameters constrained |
| $S = 1.09$ | $\Delta\rho_{max} = 0.59$ e Å$^{-3}$ |
| 5535 reflections | $\Delta\rho_{min} = -0.51$ e Å$^{-3}$ |
| 322 parameters | |

### Compound (II)

*Crystal data*

| | |
|---|---|
| $[Cd(C_{24}H_{32}N_6)_2(H_2O)_2](NCSe)_2\cdot 2H_2O$ | $\beta = 100.168\ (2)^\circ$ |
| $M_r = 1203.54$ | $V = 2566.2\ (3)$ Å$^3$ |
| Monoclinic, $P2_1/c$ | $Z = 2$ |
| $a = 6.9147\ (5)$ Å | Mo $K\alpha$ radiation |
| $b = 20.4704\ (14)$ Å | $\mu = 1.90$ mm$^{-1}$ |
| $c = 18.4190\ (15)$ Å | $T = 213$ K |
| | 0.21 × 0.12 × 0.09 mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII area-detector diffractometer | 13671 measured reflections |
| Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 2003) | 5235 independent reflections |
| $T_{min} = 0.012$, $T_{max} = 0.847$ | 3469 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.050$ |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.053$ | 4 restraints |
| $wR(F^2) = 0.128$ | H-atom parameters constrained |
| $S = 1.07$ | $\Delta\rho_{max} = 0.89$ e Å$^{-3}$ |
| 5235 reflections | $\Delta\rho_{min} = -0.97$ e Å$^{-3}$ |
| 322 parameters | |

For both structures, C-bound H atoms were treated as riding in geometrically idealized positions, with triazole C—H = 0.94 Å and aliphatic C—H = 0.98 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were found in intermediate difference Fourier maps and initially included with a tight O—H restraint [0.8500 (1) Å]. In the final

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**Table 1**
Hydrogen-bond geometry (Å, °) for (I).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*W*···O2 | 0.85 | 1.85 | 2.689 (2) | 167 |
| O1—H2*W*···N2$^{\mathrm{v}}$ | 0.85 | 2.02 | 2.868 (2) | 171 |
| O2—H3*W*···S1$^{\mathrm{v}}$ | 0.85 | 2.40 | 3.2334 (11) | 169 |
| O2—H4*W*···N7 | 0.85 | 1.97 | 2.817 (4) | 173 |
| C1—H1···N4$^{\mathrm{ii}}$ | 0.94 | 2.41 | 3.085 (4) | 128 |

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

**Table 2**
Hydrogen-bond geometry (Å, °) for (II).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*W*···O2 | 0.85 | 1.86 | 2.703 (4) | 170 |
| O1—H2*W*···N2$^{\mathrm{v}}$ | 0.85 | 2.08 | 2.909 (4) | 163 |
| O2—H3*W*···Se1$^{\mathrm{v}}$ | 0.85 | 2.47 | 3.321 (2) | 174 |
| O2—H4*W*···N7 | 0.85 | 1.99 | 2.821 (6) | 166 |
| C1—H1···N4$^{\mathrm{ii}}$ | 0.94 | 2.44 | 3.109 (5) | 128 |

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

refinement, the positions of the water H atoms were fixed, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})$.

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3170). Services for accessing these data are described at the back of the journal.

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