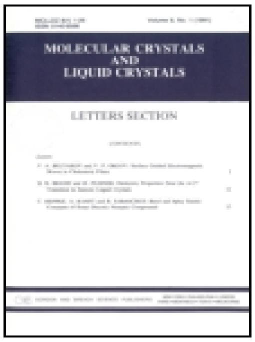

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Supramolecular Frameworks of Two Cadmium Complexes via Hydrogen-Bonding Assembly

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*Two novel complexes, $[Cd(L)(NO_3)_2(H_2O)_2]$ (**1**) and $[Cd(L)_2(NO_3)_2]$ (**2**) constructed from 3-(dimethylamino)-1-(pyridine-4-yl)prop-2-en-1-one) (L), have been synthesized and characterized by elemental analyses and single crystal X-ray diffraction. The crystal structure analysis reveals that the cadmium (II) is a seven-coordinated ion in a distorted pentagonal bipyramid environment in complex **1**, while the other Cd ion is an eight-coordinated ion in a pseudo square anti-prismatic environment in complex **2**. Both complexes assembled into 3D hydrogen-bonding frameworks based on C-H···O, O-H···O hydrogen bond linkages.*

Keywords Cadmium complexes; crystal structure; hydrogen bonds

Introduction

Recently, non-covalent supramolecular interactions and self-assemblies have attracted considerable interest and growing importance [1–6]. Cooperative interactions, such as hydrogen bonding, CH—π, and π—π stacking, play an important role in the architecture, which favors construction of higher dimensional super-molecular framework and reinforce structural stability. The hydrogen bond, as compared with other forces of interaction, has made it the most important interaction in supramolecular chemistry due to its relative strength, directionality, and ability to provide a directing force in determining molecular conformation and supramolecular arrangement in solids [7–10]. The intermolecular interactions of crystalline materials as a sub-discipline of supramolecular chemistry are very much useful and show a wide range of potential applications in gas storage device, sensor, catalysis, semiconductor, superconducting material, and optical switch, which are attractive materials for use in solar cells. The design of a number of supramolecular architectures, such as layers, ribbons, tubes, sheets, and spheres, can be achieved through N—H···O and O—H···O

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strong hydrogen bonds [11–12]. In addition to N—H···O, N—H···N, and O—H···O hydrogen bonds, it is worthy to note that weak C—H···O hydrogen bonds also play an important role in further stabilizing the 3D network structures.

In our previous work, we have reported several complexes derived from the same ligand 3-(Dimethylamino)-1-(pyridine-4-yl) prop-2-en-1-one [13–16]. Herein we report two novel 3D supramolecular cadmium complexes constructed by strong O—H···O hydrogen bonds and weak C—H···O hydrogen bonds. These studies have advanced our understanding of hydrogen bonding and interactions for the construction of structures with varied architectures.

Experimental Section

All reagents were of AR grade and used without purification. 3-(dimethylamino)-1-(pyridine-4-yl) prop-2-en-1-one was prepared by similar procedure as reported in the literature [17]. Elemental analysis was measured on a Perkin-Elmer 1400C analyzer.

Synthesis of Complexes 1 and 2

Synthesis of $[Cd(L)\ (NO_3)_2(H_2O)_2]$ *(1).* A 10-mL methanol solution of 3-(Dimethylamino)-1-(pyridine-4-yl)prop-2-en-1-one (17.6 mg, 0.1 mmol) was successively added to 20-mL methanol solution of $Cd(NO_3)_2{\cdot}H_2O$ (0.1 mmol) with stirring. The mixture was refluxed for 2 hr to obtain a clear solution, and after standing at room temperature for one week, well-shaped single crystals were obtained (yield: 40%). Anal. Calcd. for $C_{10}H_{16}CdN_4O_9$: C, 26.77; H, 3.59; N, 12.49. Found: C, 26.53; H, 3.68; N, 12.70.

Synthesis of $[Cd(L)_2(NO_3)_2]$ *(2).* Complex **2** was made in the same way as complex **1** except that the reactant ratio is 2:1 ($L{:}Cd(NO_3)_2{\cdot}H_2O$). Crystals were formed after eight days (yield: 56%). Anal. Calcd. for $C_{20}H_{24}CdN_6O_8$: C, 40.79; H, 4.11; N, 14.27. Found: C, 41.05; H, 4.02; N, 13.97.

X-ray Crystallography

Data collection for complexes **1** and **2** was performed on a Bruker SMART 1K CCD diffractometer at 291 K by employing graphite monochromatized $MoK_{a\text{-}}$ radiation ($\lambda = 0.71073$ Å). The data were collected using SMART and reduced by the program SAINT [18]. The structure was solved by the direct method and refined by full-matrix least squares fitting on "F^2_{obs}" by SHELXTL-PC [19]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The C–H hydrogen atoms were positioned geometrically and refined using a riding model with $d(CH_{aro}) = 0.95$ Å, $U_{iso} = 1.2U_{eq}$ (C) for aromatic, and 0.98 Å, $U_{iso} = 1.2U_{eq}$ (C) for CH_3. The O–H hydrogen atoms were localized by difference Fourier maps and refined by fixing the bond lengths at 0.840 (1) Å. The crystallographic data for complexes **1** and **2** are listed in Table 1.

Results and Discussion

Structural Descriptions of Complexes 1 and 2

Single-crystal X-ray structural analysis of complex **1** indicates pentagonal bipyramid geometry with two axial positions occupied by one water molecule and one nitrate, with the O3-Cd1-O8 angle of 154.94 (10) (shown in Fig. 1). Five coordination sites of the basal

Table 1. Crystal data and structure refinement parameters for **1** and **2**

Complex	**1**	**2**
Formula	$C_{10}H_{16}CdN_4O_9$	$C_{20}H_{24}CdN_6O_8$
MR	448.67	588.85
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$
a (Å)	7.5059 (4)	9.3248 (8)
b (Å)	10.0787 (8)	16.0113 (13)
c (Å)	11.8196 (8)	16.3315 (14)
α (deg)	81.352 (2)	90.00
β (deg)	76.5660 (10)	100.328 (2)
γ (deg)	71.4400 (10)	90.00
V (Å)^3	821.62 (10)	2398.8 (4)
Z	2	4
ρ_{cad} (g cm^{-3})	1.814	1.630
μ (Mo Kα) (mm^{-1})	1.382	0.968
Temp (K)	291 (2)	291 (2)
F (000)	448	298.0
Data collected	4977	5205
Unique data (R_{int})	2881 (0.022)	5205 (0.036)
Observed data [I > 2σ (I)]	2573	4650
Final R [I > 2σ (I)]	0.0283	0.0532
wR	0.0621	0.1273
S	1.04	1.183
$\Delta\rho_{\mathrm{min}}$, $\Delta\rho_{\mathrm{max}}$[e Å^{-3}]	–0.37, 0.44	–0.39, 0.73

pentagon are occupied by four O-atoms and one N-atom, of which two O-atoms are from nitrate, another from a water molecule, and remainder O-atom and one N-atom from ligand (L). It is worthy to note that two nitrate molecules adopt different coordination modes: monodentate (nitrate 1) and chelating bidentate (nitrate 2) (see Scheme 1). Selected bond lengths and bond angles are given in Table 2.

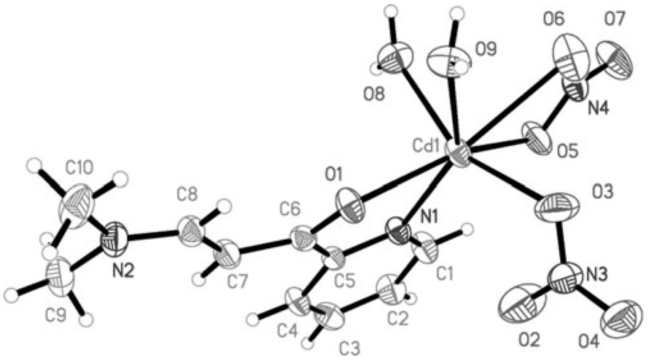
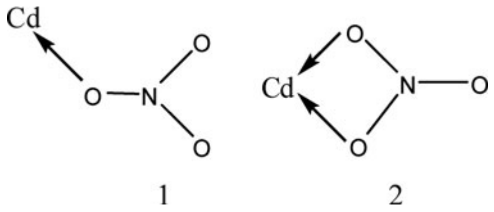


Figure 1. The ORTEP view coordination environment around the Cd(II) atom of complex **1.**



Scheme 1. Coordination modes of nitrate groups in complex **1.**

Complex **2** crystallizes in P2(1)/n space group (Fig. 2), comprising one Cd atom, two ligands, and two nitrates. The Cd^{2+} center is eight coordinated displaying a pseudo square anti-prismatic structure. One nitrogen atom and one oxygen atom from one ligand, and two oxygen atoms from one nitrate were coordinated and taken on four vertexes of the structure to form the top plane, and the other four vertexes were occupied symmetrically to form the bottom plane. Both the nitrates adopt the second coordination mode as shown in Scheme 1. Selected bond lengths and bond angles are given in Table 2.

Table 2. Selected bond distances (Å) and angles (°)

		Complex **1**			
Cd−O1	2.317 (2)	Cd1−O3	2.353 (3)	Cd1−O5	2.405 (3)
Cd1−O6	2.649 (3)	Cd1−O8	2.333 (3)	Cd1−O9	2.300 (2)
Cd1−N1	2.335 (3)	O1−Cd1−O3	98.20 (10)	O1−Cd1−O5	152.54 (9)
O1−Cd1−O6	157.07 (8)	O1−Cd1−O8	95.58 (9)	O1−Cd1−O9	81.91 (9)
O1−Cd1−N1	70.07 (8)	O3−Cd1−O5	94.53 (11)	O3−Cd1−O6	78.79 (11)
O3−Cd1−O8	154.94 (10)	O3−Cd1−O9	81.99 (10)	O3−Cd1−N1	117.47 (11)
O5−Cd1−O6	49.78 (9)	O5−Cd1−O8	82.39 (10)	O5−Cd1−O9	124.10 (10)
O5−Cd1−N1	82.46 (9)	O6−Cd1−O8	80.37 (10)	O6−Cd1−O9	75.16 (9)
O6−Cd1−N1	131.63 (8)	O8−Cd1−O9	79.35 (9)	O8−Cd1−N1	86.91 (10)
		Complex **2**			
Cd1−O7	2.322 (3)	Cd1−N3	2.328 (4)	Cd1−O8	2.347 (3)
Cd1−N5	2.372 (3)	Cd1−O2	2.40 (3)	Cd11−O4	2.432 (15)
Cd1−O5	2.501 (14)	Cd1−O1	2.54 (3)	O1−Cd1−O2	50.9 (13)
O1−Cd1−O7	85.2 (9)	O1−Cd1−O8	124.7 (8)	O1−Cd1−N3	94.9 (14)
O1−Cd1−N5	166.2 (9)	O2−Cd1−O7	124.9 (11)	O2−Cd1−O8	74.6 (8)
O2−Cd1−N3	81.3 (19)	O2−Cd1−N5	142.8 (10)	O4−Cd1−O5	50.8 (9)
O4−Cd1−O7	74.3 (5)	O4−Cd1−O8	129.5 (5)	O4−Cd1−N3	143.8 (5)
O4−Cd1−N5	91.0 (6)	O5−Cd1−O7	124.6 (7)	O5−Cd1−O8	87.2 (6)
O5−Cd1−N3	162.0 (8)	O5−Cd1−N5	100.9 (8)	O7−Cd1−O8	142.45 (10)
O7−Cd1−N3	69.82 (11)	O7−Cd1−N5	84.72 (11)	O8−Cd1−N3	84.19 (11)
O8−Cd1−N5	68.45 (11)	N3−Cd1−N5	90.58 (12)	O2−Cd1−O4	116.4 (16)
O2−Cd1−O5	81 (2)	O4−Cd1−O1	77.2 (15)	O5−Cd1−O1	77.3 (17)

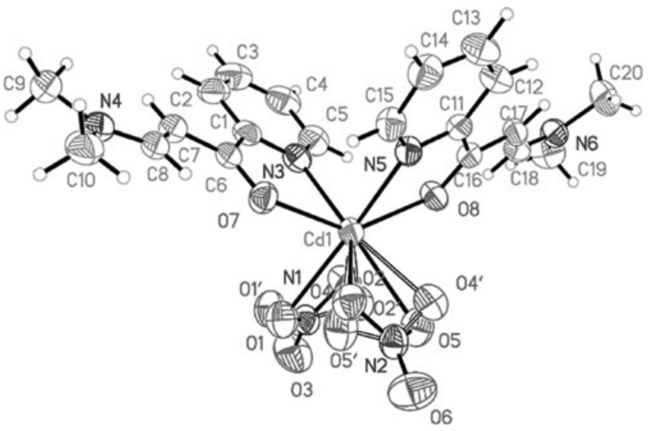


Figure 2. The ORTEP view coordination environment around the Cd(II) atom of complex **2.**

Structure Analysis of Hydrogen-bonded Supramolecules

Both oxygen atoms and aromatic hydrogens of the ligand participate in intermolecular hydrogen bonding, leading to the construction of novel hydrogen-bonded supramolecules. Hydrogen bond lengths and angles for complexes **1** and **2** are listed in Table 3.

For complex **1**, the packing structure shows a three-dimensional supramolecular network formed via intermolecular C—H···O, O—H···O hydrogen bonds weak stacking interactions. First, 1D hydrogen-bonded network is linked via hydrogen bonds A, O8—H8···O2

Table 3. Hydrogen bond distances and angles

D—H···A	H···A	∠DHA	A
		Complex **1**	
A: O8—H8···O2	1.9600	174.00	−1+x, y, z
B: O9—H9···O4	2.4900	129.00	1−x, 1−y, −z
C: C3—H3···O7	2.1400	174.00	1−x, 1−y, −z
D:O8—H8···O7	1.9200	179.00	1−x, 1−y, 1−z
E: O9—H9···O1	2.0500	179.00	−1+x, y, z
C1—H3···O5	2.4100	127.00	
O8— H8D···O5	2.4500	174.00	1+x, −1+y, z
C8— H8···O1	2.4800	101.00	
C9—H9B···O8	2.6000	143.00	1−x, −y, 1−z
		Complex **2**	
A:C19—H19···O6	2.4400	101.00	
B:C14—H14···O2	2.2300	141.00	3/2−x, 1/2+y, 3/2−z
C:C17—H17···O4	2.4500	159.00	−1+x, y, z
D:C20—H20···O4	2.4700	165.00	3/2−x, −1/2+y, 3/2−z
C18—H18···O8	2.4200	102.00	
C8—H8···O7	2.5900	142.00	1/2+x, 1/2−y, 1/2+z
C10—H10···O5	2.3000	151.00	3/2−x, −1/2+y, 3/2−z

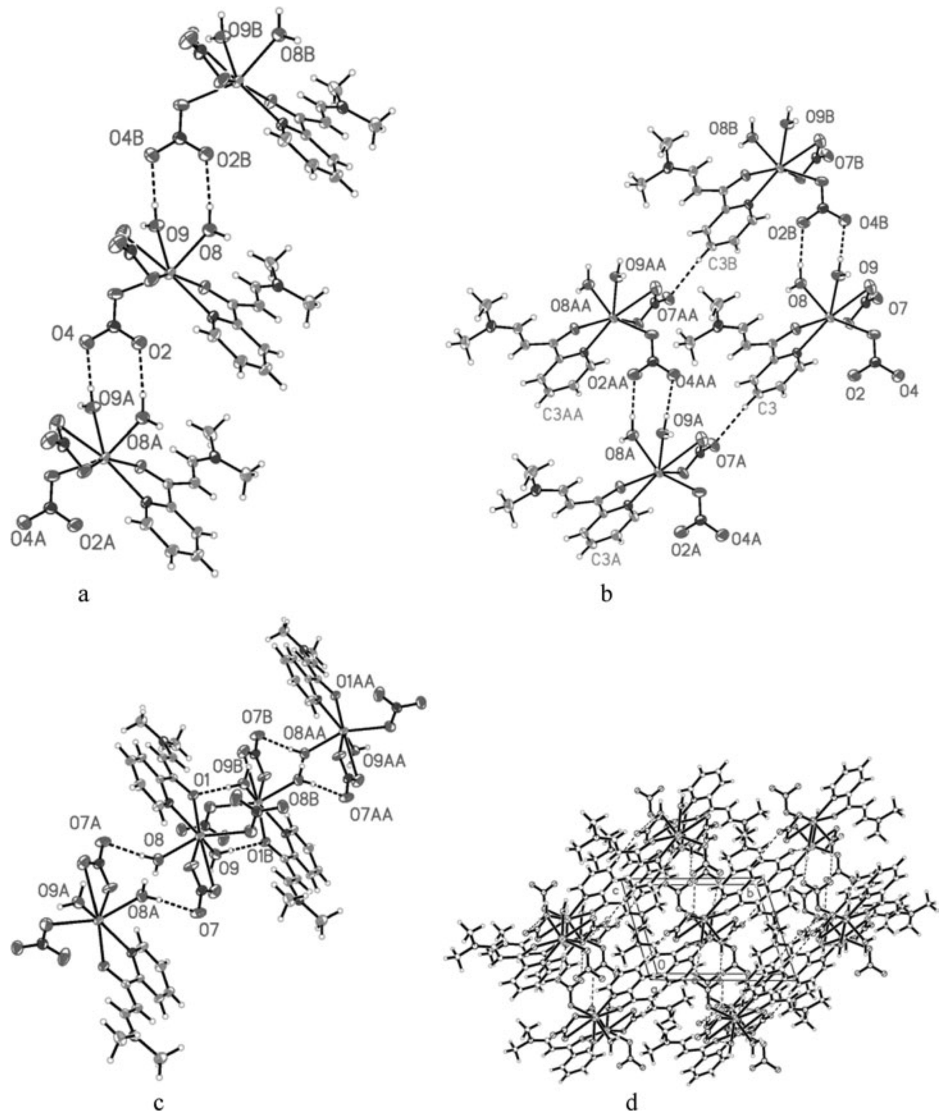


Figure 3. (a) One-dimension chain of **2** formed through hydrogen bonds A and B along *b*-axis; (b) two-dimensional structure formed by hydrogen bond C along *c*-axis; (c) hydrogen bonding interactions of D and E long *b*-axis; (d) three-dimensional structure formed by C—H···O and O—H···O hydrogen bonds.

and B, O9—H9···O4 along *b*-axis (see Fig. 3(a)). The non-coordinated oxygen atom O2 of nitrate 1 and hydrogen H8 of the coordinated water molecule are engaged in hydrogen A; the formation of hydrogen B is similar to hydrogen A. Then 1D hydrogen-bonded network is connected and spread through *c*-axis by hydrogen bond C, C3—H3···O7, which is implicated with the non-coordinated oxygen atom O7 of nitrate 2 and aromatic hydrogen atom H3 *para* to the nitrogen atom of the pyridyl cycle (Fig. 3(b)). Further, the resulted 2D networks are eventually assembled into 3D supramolecules via hydrogen bond D, O8—H8···O7, and E, O9—H9···O1 (Fig. 3(d)). As shown in Fig. 3(c), hydrogen bond D is involved with the

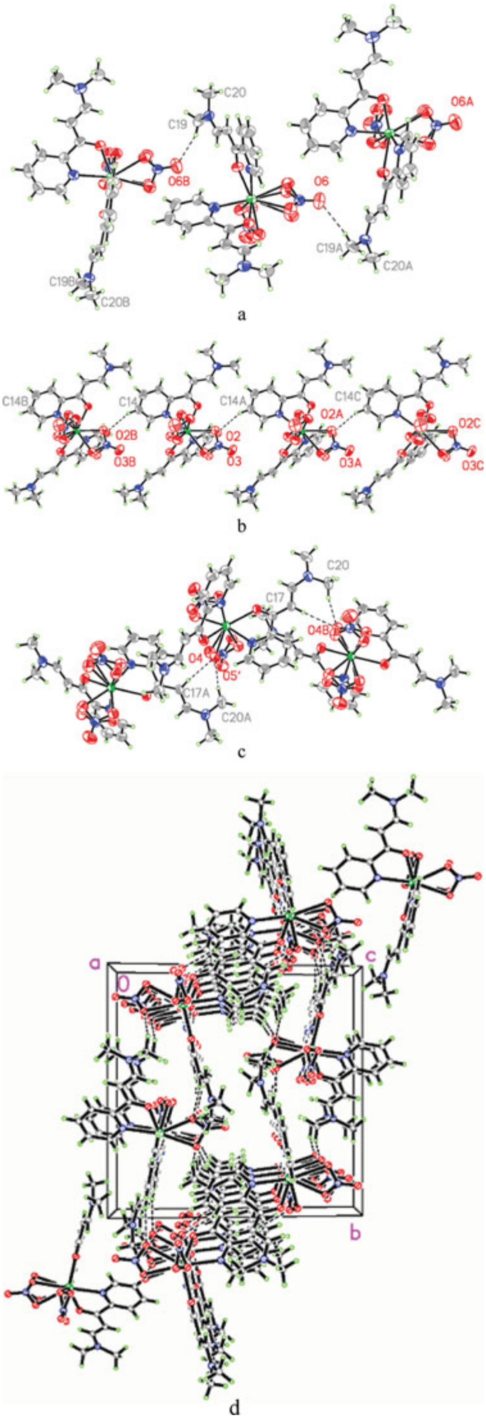


Figure 4. (a) One-dimension chain of **2** formed through hydrogen bond A along *a*-axis; (b) Two-dimensional structure formed by hydrogen bond B along *b*-axis; (c) hydrogen bonding interactions of C and D long *c*-axis; (d) Three-dimensional structure formed by C—H···O hydrogen bonds.

hydrogen atom H8 of the coordinated water molecule and the non-coordinated oxygen atom O7 of nitrate 2. Hydrogen bond E is formed between oxygen atom O1 of the ligand and the hydrogen atom H9 of the coordinated water molecule. Moreover, there are other types of hydrogen bonds, such as C1—H3···O5, O8—H8D···O5, C8—H8···O1, and C9—H9B···O8, and the existence of these reinforce the structural stability of complex **1**. It is very interesting to note that the coordinated water molecule play an important role in the formation of hydrogen bonds; especially the water molecule-involved oxygen atom O8 participates in four types of hydrogen bonds, that is O8—H8C···O2, O8—H8D···O5, O8—H8D···O7, and C9—H9B···O8.

For complex **2**, different from complex **1**, there is only one kind of hydrogen bonds, C—H···O, and the hydrogen bonds along *a*, *b*, and *c* axes are shown in Figs. 4(a), (b), and (c0 respectively. As shown in Fig. 4(a), hydrogen bond A, C19—H19···O6, is involved in the non-coordinated oxygen atom O6 of the nitrate and hydrogen atom H19 in $N(CH_3)_2$-group of the ligand, the hydrogen bonds A are spread through *a*-axis to produce 1D hydrogen-bonded network. The 1D chains are further connected to each other by the assistance of hydrogen bond B (C14—H14···O2) between the coordinated oxygen atom O2 of the nitrate and the aromatic *meta* hydrogen H14 that ultimately results in 2D network propagating along the crystallographic *b*-axis. As a consequence, 2D networks are stacked to each other, resulting in the formation of 3D hydrogen-bonded supramolecules via hydrogen bond C, C17—H17···O4, and hydrogen bond D, C20—H20···O4 (Fig. 4(d)). It is interesting to note that the non-coordinated oxygen atom O4 acts as a hydrogen-bond acceptor in both hydrogen bonds C and D. Moreover, there is another type of intermolecular hydrogen bond C10—H10···O5, which reinforces structural stability to complex **2**.

Conclusions

In conclusion, two unique Cd complexes have been synthesized by using multifunctional ligand 3-(Dimethylamino)-1-(pyridine-4-yl) prop-2-en-1-one). X-ray crystallographic analysis reveals that both oxygen atom and aromatic hydrogens of the ligand are involved in intermolecular hydrogen-bonding to form 3D hydrogen-bonded molecular frameworks, which proved that non-covalent interactions, such as H-bond, play an important role in instructing and directing the supramolecular architectures.

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Supplementary Materials

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center with CCDC deposition numbers 940389 and 948643 for complexes **1** and **2** respectively. Copies of this information may be obtained free of charge at www.ccdc.cam.ac.uk/ data request.cif.

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