

Synthesis, crystal structure and photo luminescent property of a 3D metal-organic hybrid of Cd(II) constructed by two different bridging carboxylate

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Abstract. A solvothermal reaction of cadmium (II) nitrate with succinic acid and isonicotinic acid creates a novel 3D metal-organic framework, $[\text{Cd}_3(\text{isonicotinate})_2(\text{suc})_2]_n(\mathbf{1})$. Single crystal X-ray structure determination reveals that complex **1** posses two crystallographically independent Cd(II) centres. The succinate anion acts here as a heptadentate ligand and binds five Cd(II) centre simultaneously. The heptacoordinated Cd(II) centres are oxo-bridged by succinate moiety and the hexacoordinated metal centres are terminally connected through four different succinate moiety to make the overall 2D sheet arrangement. In unit cell, the ratio of hexadentate Cd(II) and heptadentate Cd(II) is 1:2. The new compound was also characterized by luminescence spectra and compared with the luminescence spectra of the pure isonicotinic acid.

Keywords. Metal-organic hybrid; bridging ligand; X-ray diffraction; cadmium (II); luminescence study.

1. Introduction

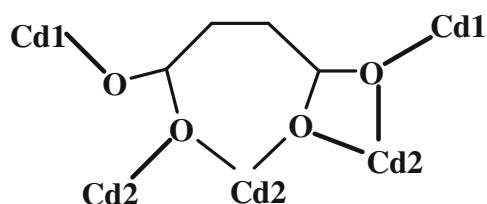
The field of metal-organic frameworks (MOFs) has attracted more interest because of their elegant framework topologies as well as their potential applications in gas storage,^{1–5} catalysis,^{6–9} separation,^{10–12} ion exchange^{13–15} and several optoelectronic¹⁶ as well as magnetic applications.^{17–19} There are many factors important for the rational design of MOFs, such as the shape and binding mode of the bridging building block, geometry of metal ions, the spacer linkages,^{20–23} binding sites,²⁴ etc. In spite of several systematic researches in this field, the role of these factors in the formation of MOFs, still is a challenge for understanding. In this aspect, carboxylates are often employed as bridging ligands to construct metal-organic frameworks^{25–28} due to their versatile coordination modes and high structural stability. Many dicarboxylates like terephthalate, fumarate, isophthalate, glutarate, adipate, malonate, etc.^{29–34} are very useful ligand in this purpose. Among these, succinate dianion^{35–37} is quite useful to create structural diversity due to its moderately longer spacer length and flexibility. These two factors may be responsible for the existence of enormous binding modes of succinate among the dicarboxylates (supporting information; scheme S1). The versatility of succinate as a ligand is observed to be more, not only by the fact that

it contains two carboxylate groups, but also by the fact those are located in the 1,4 position, which can adopt a pentadentate binding modes (scheme 1).

However, unsymmetrical, bifunctional bridging ligand,^{38–40} isonicotinate ion, which has also different coordination modes, gives various interesting frameworks. Moreover, isonicotinic acid shows extrinsic luminescent property due to the conjugation present in the system. The metal framework generated by coordinating any diamagnetic metal with isonicotinate ion also exhibit characteristic luminescence property. But succinic acid has no luminescent property as well as their metal framework also does not exhibit any luminescent property due to the unavailability of conjugation in succinate. Luminescent materials^{41,42} can be prepared by reaction of d^{10} -metal ion (diamagnetic) with fluorescence active ligands because of their potential applications as fluorescent sensors or in light-emitting devices.^{43–45}

Thus to combine the effect of structural diversity imposed by succinate, and the luminescent property by the isonicotinate; here we have synthesized the compound of Cd(II) with mixed carboxylate by hydrothermal condition. The succinate anion acts here as a heptadentate ligand and binds five Cd(II) centre simultaneously. The heptacoordinated Cd(II) centres are oxo-bridged by succinate moiety and the hexacoordinated metal centres are terminally connected through four different succinate moiety to make the overall 2D sheet arrangement.

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Scheme 1. Binding mode of succinate in compound **1**.

2. Experimental

2.1 Materials

All the reagents and solvents were commercially available and used as received without any further purification. High purity cadmium (II) nitrate tetrahydrate, succinic acid, isonicotinic acid were obtained from the Aldrich Chemical Co.

2.2 Synthesis of $[Cd_3(\text{isonicotinate})_2(\text{suc})_2]_n$ (**1**)

An aqueous solution (15 mL) of isonicotinic acid (0.123 g, 1.0 mmol), succinic acid (0.118 g, 1.0 mmol) and NaOH (0.060 g, 1.5 mmol) were mixed together. After that, a methanolic solution (7 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (0.462 g, 1.5 mmol) was added slowly to this mixture with constant stirring, which was continued for half an

hour. Then the reaction mixture was placed in Teflon-lined stainless steel vessel, heated to 130°C for 2 days and then slowly cooled to room temperature over 24 h. After cooling, light yellow crystal was obtained. The crystal was filtered off and washed several times with water (yield 43%). Anal. Calc. for $C_{20}H_{16}N_2O_{12}Cd_3$: C 29.53, H 1.98, N 3.44. Found: C 29.56, H 1.94, N 3.41. IR spectra (in cm^{-1}) $\bar{\nu}$: 1014, 1066, 3448, 2914, 2362, 1604, 1546, 1408, 1293, 1213, 1176.

2.3 Physical measurements

Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a PerkinElmer 240C elemental analyzer. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were taken on KBr pellet, using Perkin–Elmer Spectrum BX-II IR spectrometer. Emission spectra were recorded on a Perkin–Elmer LS55 fluorescence spectrophotometer.

2.4 X-ray crystallography

The single crystal of compound **1** was mounted on a thin glass fibre with commercially available super glue. X-ray single crystal data collection of **1** were performed

Table 1. Crystallographic and structural refinement parameters for $[Cd_3(\text{isonicotinate})_2(\text{suc})_2]_n$.

Empirical formula	$C_{20}H_{16}Cd_3N_2O_{12}$
Formula weight	813.58
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	7.6120(5)
<i>b</i> (Å)	9.0450(6)
<i>c</i> (Å)	9.4890(6)
$\alpha/^\circ$	64.536(3)
$\beta/^\circ$	86.926(3)
$\gamma/^\circ$	69.765(3)
<i>V</i> (Å ³)	549.95(7)
<i>Z</i>	1
<i>D_c</i> (g cm ⁻³)	2.457
<i>M</i> (mm ⁻¹)	2.947
<i>F</i> (000)	390
θ range (°)	2.4–27.7
Reflections collected	8698
Unique reflections	2519
Reflections <i>I</i> > 2σ(<i>I</i>)	2493
<i>R_{int}</i>	0.036
Goodness-of-fit on <i>F</i> ²	1.20
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>)) ^(a)	0.0493
<i>wR</i> 2(<i>I</i> > 2σ(<i>I</i>)) ^(a)	0.1513
$\Delta\rho$ max/min/e Å ³	–1.25, 2.99

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR_2 = \frac{[\sum (w(F_o^2 - F_c^2))^2]}{\sum w(F_o^2)^2}^{1/2}$$

Table 2. Selected bond lengths (Å) and bond angles (°) for $[Cd_3(\text{isonicotinate})_2(\text{suc})_2]_n$.

Cd1–O3	2.282(7)	Cd1–O6 ^b	2.218(8)
Cd1–O4 ^d	2.213(8)	Cd1–O4 ^e	2.213(8)
Cd1–O6 ^c	2.218(8)	Cd1–O3 ^a	2.282(7)
Cd2–O1	2.369(7)	Cd2–O2	2.433(7)
Cd2–N1	2.359(7)	Cd2–O5 ^f	2.270(7)
Cd2–O1 ^g	2.413(7)	Cd2–O2 ^h	2.516(6)
Cd2–O3 ^h	2.470(7)	Cd2–O2–Cd2 ^h	112.0(3)
O3–Cd1–O6 ^b	94.1(3)	O3–Cd1–O4 ^d	85.1(3)
O3–Cd1–O4 ^e	94.9(3)	O3–Cd1–O6 ^c	85.9(3)
O3–Cd1–O3 ^a	180.00	O4 ^d –Cd1–O6 ^b	92.0(4)
O4 ^e –Cd1–O6 ^b	88.1(4)	O6 ^b –Cd1–O6 ^c	180.00
O3 ^a –Cd1–O6 ^b	85.9(3)	O4 ^d –Cd1–O4 ^e	180.00
O4 ^d –Cd1–O6 ^c	88.1(4)	O3 ^a –Cd1–O4 ^d	94.9(3)
O4 ^e –Cd1–O6 ^c	92.0(4)	O3 ^a –Cd1–O4 ^e	85.1(3)
O3 ^a –Cd1–O6 ^c	94.1(3)	O1–Cd2–O2	81.6(2)
O1–Cd2–N1	84.2(2)	O1–Cd2–O5 ^f	92.2(3)
O1–Cd2–O1 ^g	76.1(2)	O1–Cd2–O2 ^h	148.9(2)
O1–Cd2–O3 ^h	152.8(2)	O2–Cd2–N1	82.7(2)
O2–Cd2–O5 ^f	82.4(3)	O1 ^g –Cd2–O2	153.3(2)
O2–Cd2–O2 ^h	68.0(2)	O2–Cd2–O3 ^h	118.8(2)
O5 ^f –Cd2–N1	165.1(3)	O1 ^g –Cd2–N1	80.5(2)
O2 ^h –Cd2–N1	85.3(2)	O3 ^h –Cd2–N1	81.2(2)
O1 ^g –Cd2–O5 ^f	112.7(3)	O2 ^h –Cd2–O5 ^f	90.5(3)
O3 ^h –Cd2–O5 ^f	107.4(3)	O1 ^g –Cd2–O2 ^h	130.7(2)
O1 ^g –Cd2–O3 ^h	79.0(2)	O2 ^h –Cd2–O3 ^h	52.1(2)
Cd1–O3–Cd2 ^h	104.8(2)	Cd2–O1–Cd2 ^g	104.0(3)

Symmetry code: a = 3 – *x*, –2 – *y*, 1 – *z*; b = 1 + *x*, –1 + *y*, 1 + *z*; c = 2 – *x*, –1 – *y*, –*z*; d = 1 + *x*, *y*, *z*; e = 2 – *x*, –2 – *y*, 1 – *z*; f = *x*, *y*, 1 + *z*; g = 1 – *x*, –1 – *y*, 1 – *z*; h = 2 – *x*, –1 – *y*, 1 – *z*.

at room temperature using Bruker APEX II diffractometer, equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were integrated using SAINT⁴⁶ program and the absorption corrections were made with SADABS. The structures was solved by SHELXS 97⁴⁷ using Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F² using SHELXL-97⁴⁸ with anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen fixed geometrically by HFIX command and placed in ideal positions. All calculations were carried out using SHELXL 97, SHELXS 97, PLATON v1.15,⁴⁹ ORTEP-3v2,⁵⁰ and WinGX system Ver-1.80.⁵¹

The coordinates, anisotropic displacement parameters, and torsion angles of compound **1** are submitted as Supporting Information in CIF format. Data collection and structure refinement parameters and crystallographic data of compound **1** are given in table 1. The selected bond lengths, bond angles are given in table 2.

3. Results and discussion

3.1 Synthesis

Compound **1** has been synthesized by hydrothermal technique in Teflon-lined stainless steel vessel, heated to 130°C for 2 days.

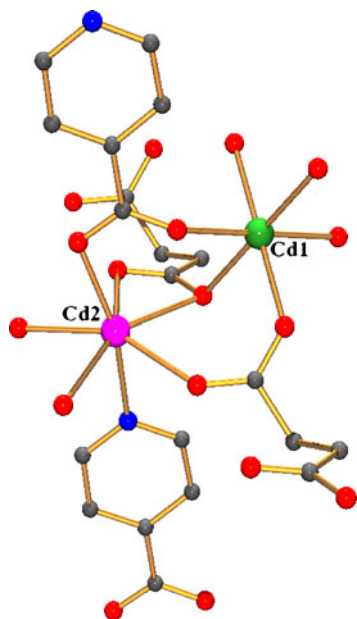
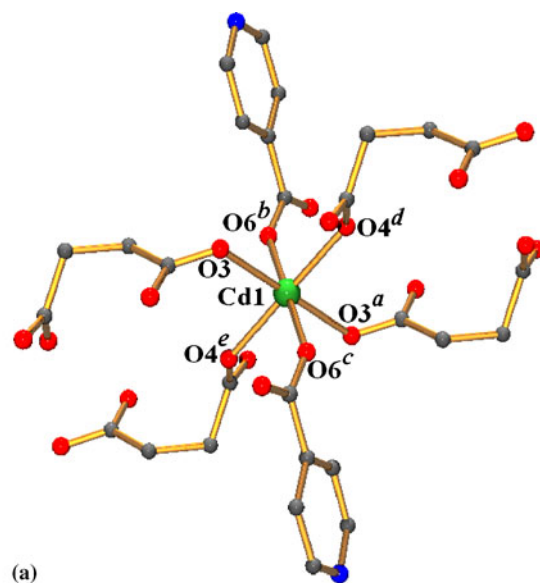


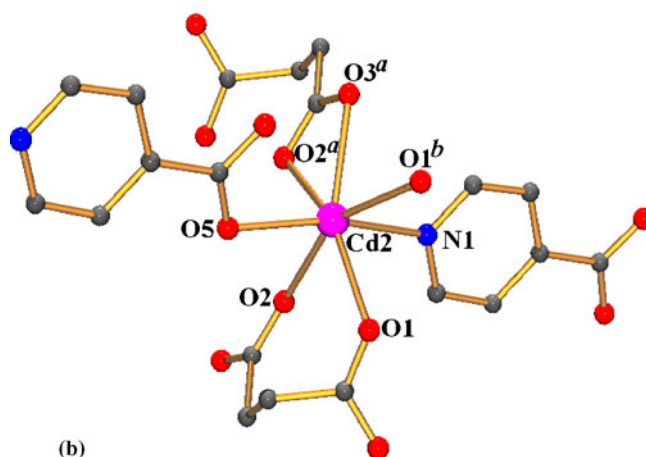
Figure 1. ORTEP drawing of hexa-coordinated Cd1 and hepta-coordinated Cd2.

3.2 Structural description of $[Cd_3(\text{isonicotinate})_2(\text{suc})_2]_n$ (**1**)

Compound **1** crystallizes in triclinic P-1 space group and the single-crystal X-ray structure analysis revealed that the formation of three-dimensional structure constituted by the bridging succinate and isonicotinate. Here, each asymmetric unit consists of two crystallographically independent Cd(II) centres. The environment of Cd1 is hexacoordinated while the Cd2 belongs to the hepta coordinated system. In this respect, the chromophore of Cd1 is CdO₆ while in Cd2 it is CdN₁O₆ (figure 1). In case of Cd1, two pairs of symmetry generated O atoms (O3, O3^a, O4^d, O4^e) coming from four different succinate creates the equatorial position and two symmetry generated O atoms (O6^b, O6^c) from two different isonicotinate ions occupies the axial position of the octahedron (figure 2a). However, the hepta-coordinated Cd2 shows distorted pentagonal bipyramidal geometry. Here the equatorial positions are occupied



(a)



(b)

Figure 2. Atom labelling diagram of (a) Cd1 and (b) Cd2.

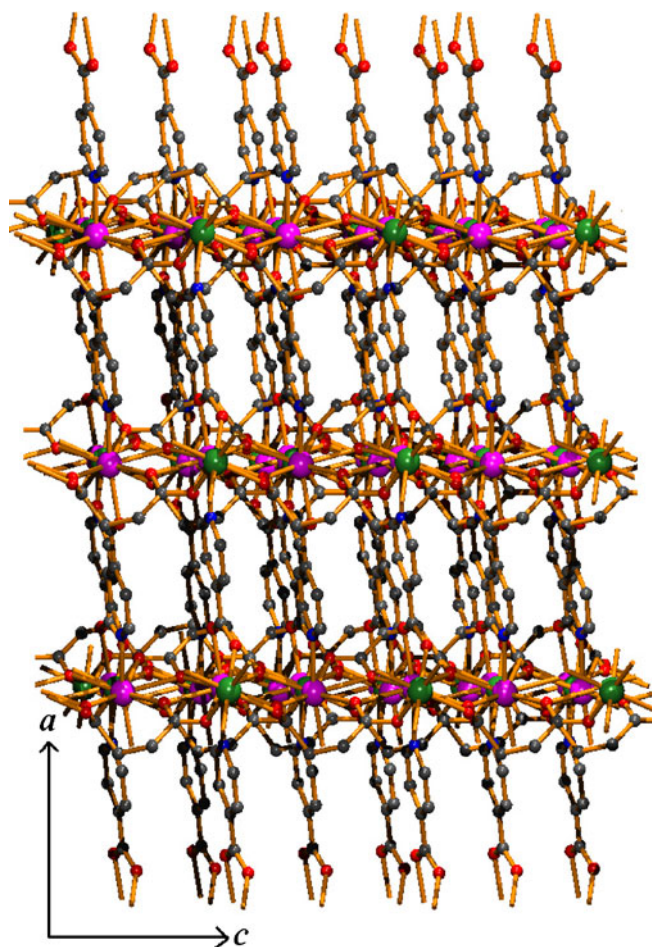


Figure 3. 3D structure of **1** viewed along *b*-axis.

by five O atoms (two pairs of symmetry generated O1, O1^b, O2, O2^a and O3^a) from three different succinate moiety with Cd–O distances varies from 2.369(7)–2.516(6) Å whereas, the axial positions are occupied by one N atom (N1) from isonicotinate and one O atom (O5) from another isonicotinate (figure 2b, table 2).

The bridging succinate as well as the bridging isonicotinate creates the overall 3D structure (figure 3) connecting Cd1 and Cd2 in different fashion. In this 3D structure, the isonicotinates connected three different Cd(II) centre (one six-coordinated and two hepta-coordinated) in a ladder-like fashion (figure 4, succinates are omitted for clarity). The two coordination sites of each Cd(II) are coming from this isonicotinate.

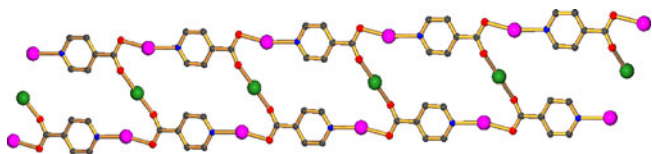


Figure 4. Isonicotinates are connect to the Cd(II) centre in a ladder-like arrangement (succinates are omitted for clarity).

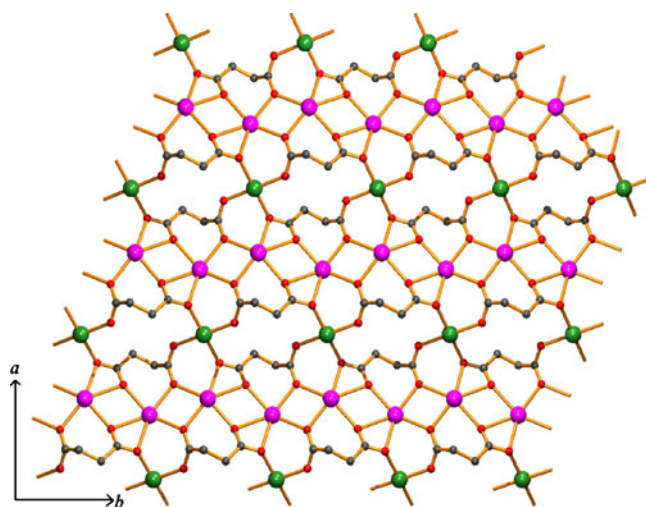


Figure 5. 2D sheet arrangements constructed by succinate moiety viewing along *ab* plane (isonicotinates are omitted for clarity).

The succinate anion acts here as a heptadentate ligand and binds five Cd(II) centre simultaneously (scheme 1, figure 5, isonicotinates are omitted for clarity) out of those, three are Cd2 and the rest two are Cd1. The hepta-coordinated Cd2 centres are oxo-bridged by succinate moiety and the hexa-coordinated Cd1 centres are terminally connected through four different succinate moiety to make the overall 2D sheet arrangement in *ab* plane (figure 5). It is interesting to note that the close integrity of the Cd2, created by the succinate ligand produce the unit cell with double number of Cd2 with respect to Cd1. In the construction of the overall structure it is also (figures 4 and 5) visible that there are double number of heptadentate Cd2 with respect to hexadentate Cd1.

4. Luminescence property

In the solid state, the fluorescence emission spectrum of the isonicotinic acid ligand shows emission bands at ~423 nm (very strong) and ~486 nm (weak) when it is excited at 325 nm (figure 6). This strong emission is due to the intra-ligand charge-transfer transition through the delocalized carboxylic group present in the ligand, whereas the weak one may be due to the $n - \pi^*$ transition of the pyridyl N atom. The emission spectrum of complex **1** with the excitation of 325 nm was shown in figure 6. It displays only one moderately broad and low energy emission at around 441 nm, which is slightly red shifted (~18 nm) from the strong emission band of the ligand (~423 nm). The emission peaks at ~441 nm for complex **1** can be tentatively attributed to the intraligand transition which is quite similar to free ligand. The weak emission bands (486 nm, $n - \pi^*$ transition) is not

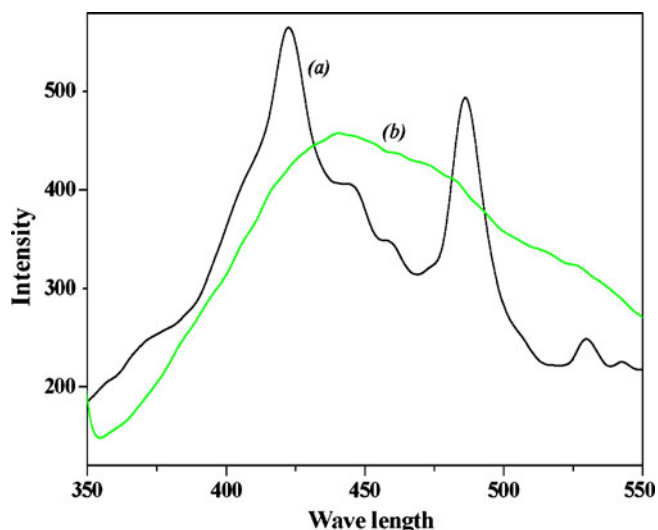


Figure 6. The solid-state photoluminescent spectra of (a) free iso-nicotinic acid (black), and (b) compound **1** (green) at room temperature.

present in this case, which corresponds the involvement of lone pair of pyridyl N atom in coordinate bond formation with Cd(II). This moderate red-shift of complex **1** corroborates the metal carboxylate bond formation that effectively increases the rigidity of the ligand and reduces the loss energy by radiation less thermal vibration. The energy difference caused by the co-ordination environment makes the red shift of the emission bands of complex **1**.

5. Conclusion

A mixed ligand three-dimensional structure of Cd(II) constituted by the bridging succinate and isonicotinate has been synthesized hydrothermally. In this structure, two crystallographically independent Cd(II) centres are present; in which one is hexa-coordinated and other is hepta-coordinated. Here, the succinate anion bridged in heptadentate fashion to connect two different Cd(II) centre and isonicotinate linked with three Cd(II) centre to form an overall 3D architecture. The bridging mode of succinate is quite uncommon here and has nicely used for the construction of 3D structure of Cd(II), where the two Cd(II) centres are differently coordinated.

Supplementary information

The different bridging modes of succinate dianion are presented as scheme **S1** in supplementary section (see www.ias.ac.in/chemsci). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC 885774

for complex **1**. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: (internet) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

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