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Original Article

Synthesis and Structural Characterization of Furan-2,5-dicarbonylbis(*N*,*N*-diethylthiourea) and its Dinuclear Cu(II) and Zn(II) Complexes

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Abstract: The condensation reaction of furan-2,5-dicarbonyl dichloride and *N*,*N*-diethylthiourea gave rise to furan-2,5-dicarbonylbis(*N*,*N*-diethylthiourea), **H_2L**. Composition and structural features of **H_2L** were studied by spectroscopic methods as well as single crystal X-ray diffraction. **H_2L** readily reacted with 1 equivalent of $CuCl_2$ or $ZnCl_2$ in MeOH with the presence of the supporting base Et_3N. Such reactions resulted in metal complexes, which were characterized by spectroscopic studies. The results indicated dinuclear neutral compounds $[M_2(L)_2]$ (M = Cu(II) or Zn(II)), in which $\{L^{2-}\}$ anions resulting from the deprotonation of **H_2L** bond to metal ions through (*S*,*O*)-donor sets of the aroylthiourea moieties.

Keywords: Aroylbis(thioureas), Cu(II) complexes, Zn(II) complexes.

1. Introduction

Benzoyl(*N*,*N*-dialkylthioureas) **HL^{ben}** are versatile ligands forming stable complexes with most transition metal ions, in which the organic ligands chiefly chelate metal ions in a bidentate (*S*,*O*) fashion (Figure 1a) [1-7]. The bipodal *iso*-phthaloylbis(*N*,*N*-dialkylthioureas) **H_2L^{iso}** with two aroylthiourea moieties is able to coordinate with two metal ions [8-13], and generate homonuclear complexes (Figure 1b) possessing large central voids suitable for cation binding.

Unfortunately, until now it has been impossible to separate inclusion complexes based on **H_2L^{iso}**. The substitution of building block with additional donor atom(s) such as pyridine for phenylene ring results in dipicolinoylbis(*N*,*N*-dialkylthiourea) **H_2L^{py}**, which facilitates the preparation of heteronuclear host-guest compounds (Figure 1b) [14-16].

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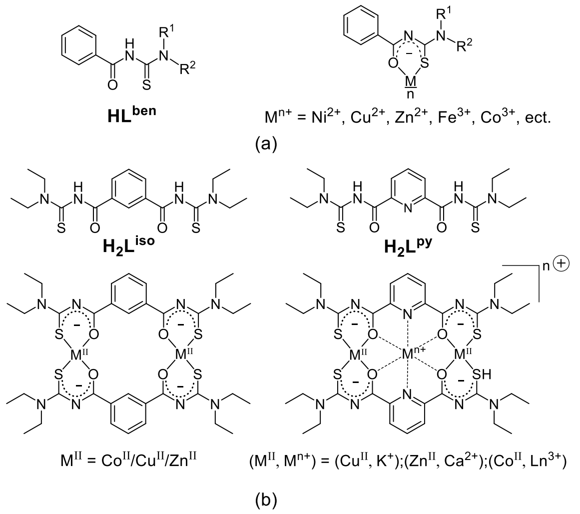
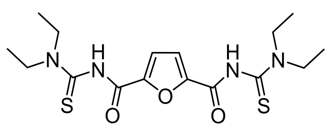


Figure 1. (a) Benzoyl(*N*,*N*-dialkylthioureas) and the major coordination fashion. (b) Aroylbis(*N*,*N*-dialkylthioureas) and their representative dinuclear complexes.

Although host-guest systems developed from $\mathbf{H_2L^{py}}$ are readily constructed, all efforts to produce the related homonuclear complexes as in the case of $\mathbf{H_2L^{iso}}$ have failed. In this context, it is worth finding new aroylbis(*N*,*N*-dialkylthioureas) which could enable the formation of both homo- and hetero-nuclear complexes. For this purpose, the building block between the two aroylthiourea moieties should possess donor atom(s) exhibiting moderate coordination ability. It is expected that the heterocyclic furan ring with mild donor character of the O atom would be a good example for such kind of building block. This expectation motivates us to synthesize the novel furan-scaffolding aroylbis(*N*,*N*-diethylthiourea) $\mathbf{H_2L}$ as well as examine its coordination ability with transition metal ions.



$\mathbf{H_2L}$

In the present work, the synthesis and structure determination of $\mathbf{H_2L}$ will be reported. Moreover, its dinuclear complexes with the divalent Cu(II) and Zn(II) ions will be discussed.

2. Materials and Methods

2.1. Materials

Furan-2,5-dicarboxylic acid (98%, Aladdin), $SOCl_2$ (99%, Aladdin), Et_3N (99%, Aladdin), DMF (99%, Aladdin), $CuCl_2 \cdot 2H_2O$ (+98%, Sigma-Aldrich) and $ZnCl_2$ (+98%, Sigma-Aldrich) were used without further purification. Solvents were distilled before use.

2.2. Physical Measurements

IR spectra were measured from KBr pellets on an IRAffinity-1S spectrometer (Shimadzu, Japan) between 400 and 4000 cm^{-1} at Department of Inorganic Chemistry, Faculty of Chemistry, VNU University of Science.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in DMSO-d_6 on an Ascend^{TM}-500MHz spectrometer at Faculty of Chemistry, VNU University of Science.

Electrospray ionization in positive mode was used to analyze the mass spectra with an MS/MS (XevoTQD mass spectrometer, Waters, USA). Samples were dissolved in a mixture of CH_2Cl_2 and MeOH, and then directly injected to the MS/MS detector by infusion mode with a flow rate of 20 μL min^{-1}. The mass spectra were recorded from 50 to 1000 amu using a cone voltage ramp from 5 to 70 eV. The scan speed was set up as 1 amu s^{-1}. Nitrogen gas (purity >99.5%) which was produced from a nitrogen generator (Parker Scientific) was employed as both drying and nebulizer gas. All MS/MS results were presented as *m*/*z*.

2.3. Synthetic Procedures

Synthesis of $\mathbf{H_2L}$: A mixture of furan-2,5-dicarboxylic acid (1.56 g, 0.01 mol), an excess amount of $SOCl_2$ (7.5 mL, 0.1 mol) and two drops of DMF was refluxed in 3 hours to obtain a clear solution. Then, the residual $SOCl_2$ was removed under low pressure to obtain furan-2,5-dicarbonyl dichloride as a colorless solid, which was used directly without any purification. The dichloride was dissolved in dry THF (30 mL) and added dropwise to cold THF solution (15 mL) of *N*,*N*-diethylthiourea (2.64 g, 0.02 mol) and Et_3N (2.8 mL, 0.02 mol).

After that, the mixture was heated up to 45℃ and stirred for 2h. After cooling to room temperature, the colorless precipitate of $Et_3N{\cdot}HCl$ was filtered off. The removal of solvent under low pressure yielded a dark brown residue. The **H_2L** was separated as colorless solid by carefully washing the residue with mixture of MeOH and Et_2O. Single crystals suitable for X-ray analysis were obtained by slow evaporation of solvent from the filtrate. Yield: 70% (2.69 g). IR (KBr, cm^{-1}): 3264 (m), 2972 (w), 2934 (w), 1694 (s), 1661 (s), 1555(s), 1464 (s), 1279 (s), 1223 (s), 1111 (m), 1016 (m), 843 (m), 750 (w), 694 (w). ^1H NMR (500 MHz, DMSO-d_6, ppm): 10.64 (s, 1H, NH); 7.41 (s, 1H, Fur); 3.96 (q, J = 7.0 Hz, 2H, CH_2); 3.56 (q, J = 7.0 Hz, 2H, CH_2); 1.26 (t, J = 7.0 Hz, 6H, CH_3); 1.20 (t, J = 7.0 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm): 178.8 (C=O); 154.0 (C=S); 147.7, 117.8 (Fur); 47.7, 47.4 (CH_2); 13.9, 11.5 (CH_3).

Syntheses of [$M_2(L)_2$] (M = Cu(II) or Zn(II)): **H_2L** (38.5 mg, 0.1 mmol) was added into solution of $CuCl_2{\cdot}2H_2O$ or $ZnCl_2$ (0.1 mmol) in 1 mL MeOH. The reaction mixtures were stirred at 40 °C for 30 min before addition of Et_3N (0.03 mL, 0.2 mmol). Precipitate with characteristic colour deposited immediately. After stirring for further 1 hour at 40 °C, the product was filtered off, washed with MeOH, and dried under low pressure.

Data for [$Cu_2(L)_2$] (**1**): Brown. Yield: ~70% (31.2 mg). IR (KBr, cm^{-1}): 2974 (w), 2931 (w), 1536 (s), 1492 (s), 1455 (m), 1399 (s), 1373 (s), 1348 (s), 1304 (s), 1262 (s), 1219 (m), 1148 (m), 1111 (m), 1074 (m), 1008 (s), 9722 (m), 880 (s), 813 (s), 767 (s), 665 (m), 6155 (w), 548 (w), 455 (m). +ESI MS (m/z): 893.19 (calcd. 893.09), 50% $[Cu_2(L)_2 + H]^+$; 931.24 (calcd. 931.05), 100% $[Cu_2(L)_2 + K]^+$.

Data for [$Zn_2(L)_2$] (**2**): Pale yellow. Yield: ~85% (38.1 mg). IR (KBr, cm^{-1}): 2977 (w), 2934 (w), 1531 (s), 1494 (s), 1457 (m), 1389 (s), 1342 (s), 1260 (s), 1216 (s), 1192 (s), 1149 (m), 1093 (s), 1007 (s), 967 (m), 877 (s), 806 (s), 761 (s), 664 (m), 545 (w), 477 (w). ^1H NMR (500 MHz, DMSO-d_6, ppm): 7.09 (s, 1H, Fur); 3.82 (q, J = 7.0 Hz, 2H, CH_2); 3.78 (q, J = 7.0 Hz, 2H, CH_2); 1.22 (t, J = 7.0 Hz, 3H, CH_3); 1.18 (t, J = 7.0 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm): 171.0 (C=O); 162.9 (C=S); 154.5, 112.6 (Fur); 46.2 (CH_2); 13.8, 13.0 (CH_3). +ESI MS (m/z): 915.14 (calcd. 915.10), 20% $[Zn_2(L)_2 + H_2O + H]^+$.

2.4. Crystallography

The intensities for the X-ray determinations of **H_2L** were collected on a Bruker D8 QUEST instrument at 140 K with Mo Kα radiation (λ = 0.71073 Å) using a TRIUMPH monochromator. Standard procedures were applied for data reduction and absorption correction [17]. Structure solution and refinement were performed with the SHELXT and SHELXL 2014/7 programs included in the OLEX2-1.5 program package [18]. More information on collections and structural calculations are provided in Table 1. CCDC 2355232 contains the supplementary crystallographic data for this paper. The data can be obtained from The Cambridge Crystallographic Data Center.

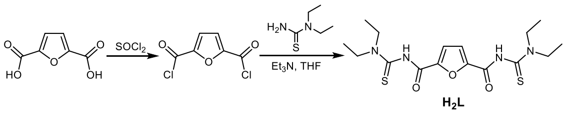
Table 1. Crystal data and structure refinement for **H_2L**

Formula	$C_{32}H_{48}N_8O_6S_4$
M_w	769.02
Crystal system	Orthorhombic
a (Å)	10.313(2)
b (Å)	21.248(4)
c (Å)	17.933(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3929.7(1)
Space group	$Pca2_1$
Z	4
D_{calc} (g cm^{-3})	1.300
μ (mm^{-1})	0.293
No. of reflections	37476
No. of independent	9364

R_{int}	0.0560
No. parameters	475
R_1/wR_2	0.0391/ 0. 0702
GOF	1.046
CCDC	2355232

3. Results and Discussion

The ligand **H_2L** was prepared following the procedure reported by Dixon and Taylor with some modifications [19] (Scheme 1). The synthesis of **H_2L** starts with conversion of furan-2,5-dicarboxylic acid into the corresponding acyl chloride by refluxing in an excess of $SOCl_2$. After that, the condensation of furan-2,5-dicarbonyl dichloride and *N*,*N*-diethylthiourea in dry THF with the presence of the supporting base Et_3N brings about **H_2L** in a good yield.



Scheme 1. Synthesis of **H_2L**.

Structural features of **H_2L** was studied by spectroscopic means including IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. In the IR spectrum of **H_2L** (Figure 2), the characteristic absorption around 1695 cm^{-1} is assigned to the C=O stretches. The weak absorptions around 2800 and 3090 cm^{-1} are ascribed to vibration of C–H bonds in alkyl groups and the furan ring, respectively. The broad band above 3100 cm^{-1} indicates appearance of NH groups, which is strongly confirmed by the broad resonance at 10.64 ppm in the ^{1}H NMR spectrum in DMSO-d_6 (Figure 3a).

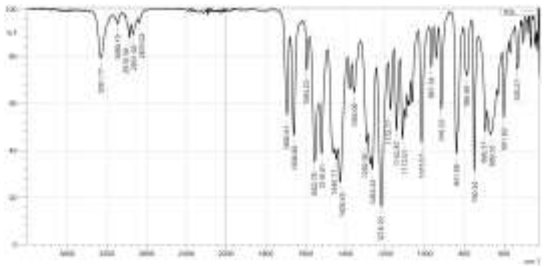
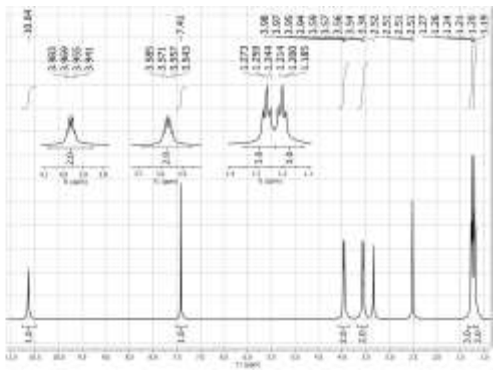
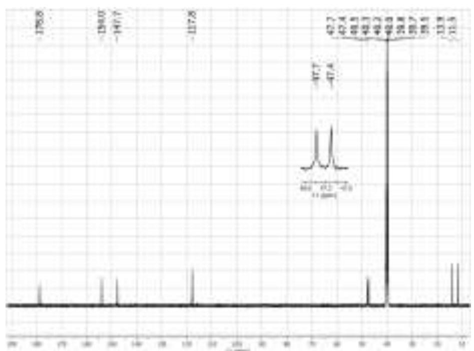


Figure 2. IR spectrum of **H_2L**.

A singlet at 7.41 ppm corresponds to resonance of protons in the furan ring, whereas aliphatic protons in the ethyl groups cause resonances in upfield region. Particularly, two triplets at 1.26 and 1.20 ppm are assigned to methyl protons, while methylene groups are responsible for two quartets at 3.96 and 3.56 ppm. The presence of two separated sets of signals for two ethyl groups are clear signs of the hindered rotation around the C(S)–NEt_2 bond, which is normally observed for aroyl-*N*,*N*-dialkylthioureas [11, 20-22]. Such structural properties could also be detected in the $^{13}C\{^1H\}$ NMR spectrum (Figure 3b) of **H_2L**. Indeed, the resonance of methylene carbon atoms appears at 47.7 and 47.4 ppm, while thoes of methyl groups are found at 13.9 and 11.5 ppm. Two signals in the range of 110-150 ppm are ascribed to aromatic carbons, whereas the carbon atoms in C=O and C=S groups show weak resonances at 178.8 and 154.0 ppm, respectively.



(a)



(b)

Figure 3. (a) ^{1}H NMR and (b) $^{13}C\{^1H\}$ NMR spectra of **H_2L** in DMSO-d_6.

The structural features deduced from spectroscopic studies are verified by X-ray crystallography. The organic compound **H_2L** crystalizes in the monoclinic non-centrometric space group *Pca*2_1 with two crystallographically independent moelcules in the asymmetric unit (Figure 4). Selected bond lengths are listed in Table 2.

The compound **H_2L** has a non-planar structure with the two *N*,*N*-diethylthiourea moieties being twisted in the same direction from the central furan ring. The bond lengths within aroylthioure moieties, namely C–O, C–S and C–NH, are in the similar ranges of those found in other aroylbis(thioureas) (Table 2) [8, 23, 24]. Whereas the C–O and C–S bond lengths fall in the expected ranges for double bonds, the C–NH distances illustrate the partial double bond character.

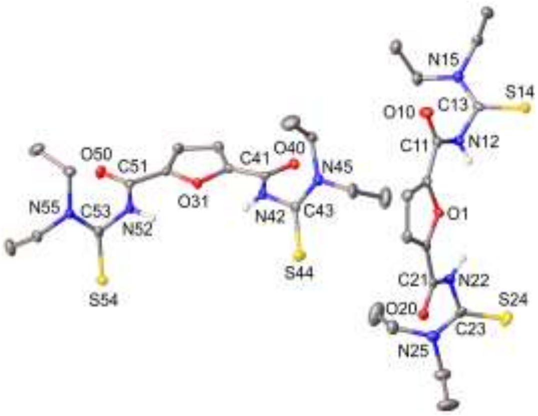
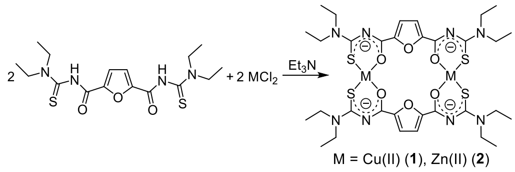


Figure 4. Molecular structure of the asymmetric unit of **H_2L**. Hydrogen atoms bonded to carbons are omitted for clarity.

Table 2. Selected bond lengths (Å) in **H_2L**

C11–O10	1.222(4)	C21–O20	1.223(4)
C11–N12	1.370(4)	C21–N22	1.376(4)
N12–C13	1.418(4)	N22–C23	1.413(4)
C13–N15	1.331(4)	C23–N25	1.335(4)
C13–S14	1.673(4)	C23–S24	1.670(3)
C41–O40	1.230(4)	C51–O50	1.226(4)
C41–N42	1.369(4)	C51–N52	1.365(4)
N42–C43	1.428(4)	N52–C53	1.430(4)
C43–N45	1.324(4)	C53–N55	1.329(4)
C43–S44	1.673(3)	C53–S54	1.668(3)

Equimolar reactions of **H_2L** with $CuCl_2$ or $ZnCl_2$ in MeOH with the presence of the supporting base Et_3N (Scheme 2) readily give rise to the corresponding metal complexes, which are directly deposited from the reaction mixtures.



Scheme 2. Syntheses of the metal complexes.

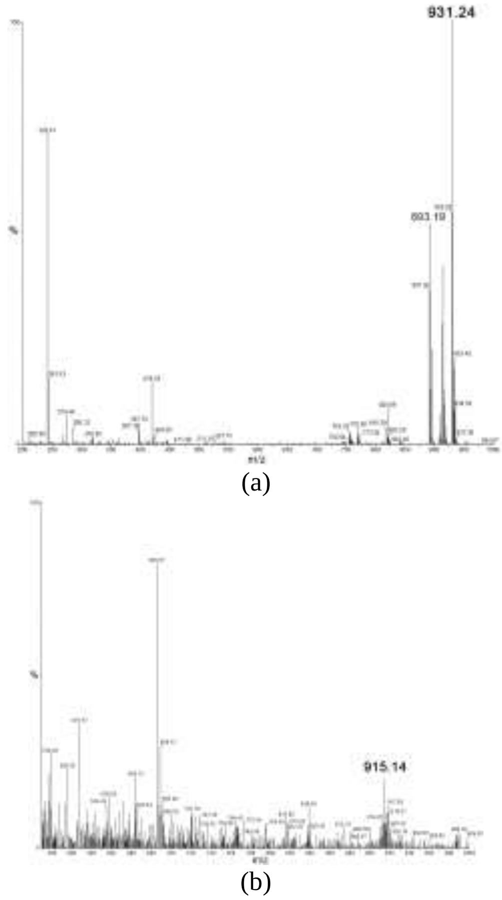
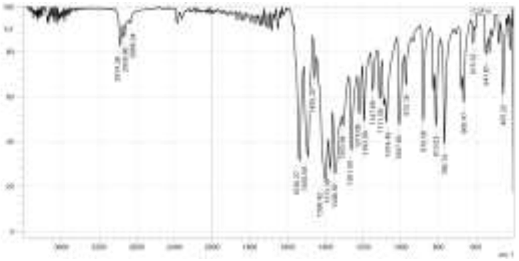


Figure 5. ESI$^+$ mass spectra of (a) **1** and (b) **2**.

With the assumption of similarity in the coordination ability of **H_2L** and **H_2L^{iso}**, it is expected that the resulting metal complexes possess the chemical compositions of $[M_2(L)_2]$ (M = Cu (**1**) or Zn (**2**)). This expectation is validated by mass spectrometry. Indeed, the ESI+ mass spectrum of **1** shows the base peak with *m*/*z* = 931.24 and a moderate signal with *m*/*z* = 893.19 (Figure 5a) assigned to the fragments $[Cu_2(L)_2 + K]^+$ (calcd. 931.05) and $[Cu_2(L)_2 + H]^+$ (calcd. 893.09) respectively. Meanwhile, the fragment of $[Zn_2(L)_2 + H_2O + H]^+$ (calcd. 915.10) could be detected at *m*/*z* = 915.14 in the spectrum of **2** (Figure 5b).

In comparision with the IR spectrum of the uncoordinated ligand $\mathbf{H_2L}$, the spectra of the metal complexes (Figure 6) show the disappearance of broad absorptions above 3100 cm^{-1} belonging to NH groups. Additionally, there are significant bathochromic shifts (about 160 cm^{-1}) of the C=O vibration. Thus, the IR data reveal the deprotonation of NH groups and the formation of *S*,*O*-chelating aroylthioureas with the typical extended π-systems during the complexation [11, 21].

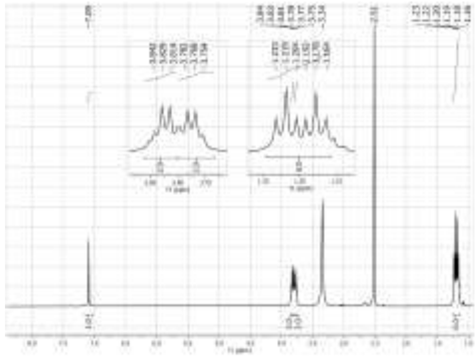


(a)

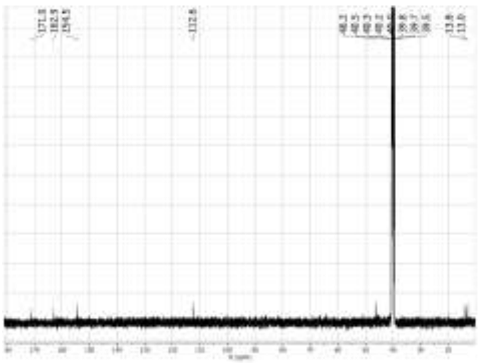
(b)

Figure 6. IR spectra of (a) **1** and (b) **2**.

Structural features of the diamagnetic Zn(II) complex **2** is also studied by NMR spectroscopy. The deprotonation of the organic ligand is validated by the absence of the most downfield and broad singlet of NH protons. The other signals in ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2** (Figure 7) show chemical shifts resembling with those found in $\mathbf{H_2L}$.



(a)



(b)

Figure 7. (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectra of **2** in DMSO-d_6.

4. Conclusion

The aroylbis(thiourea) $\mathbf{H_2L}$ based on furan-2,5-dicarboxylic acid has been synthesized and characterized by spectroscopic means such as IR, ^{1}H and $^{13}C\{^{1}H\}$ NMR, as well as X-ray crystallography. The organic ligand $\mathbf{H_2L}$ readily reacts with *d*-metal ions such as Cu^{2+} and Zn^{2+} to bring about stable metal complexes. The spectroscopic studies reveal the formation of binulcear compounds with the composition of $[M_2(L)_2]$ (M = Cu or Zn), in which the deprotonated ligands $\{L^{2-}\}$ coordinate with metal ions through (*S*,*O*)-chelators of the aroylthiourea moieties.

Acknowledgements

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