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Mixed ligand complexes of Cu(II)-2-(2-pyridyl)-benzimidazole and aliphatic or aromatic dicarboxylic acids: Synthesis, characterization and biological activity

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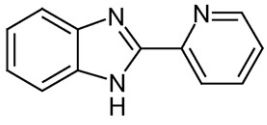
Abstract

The synthesis and structural characterization of mixed ligand complexes derived from 2-(2-pyridyl)-benzimidazole (PBI) (1ry ligand) and aliphatic or aromatic dicarboxylic acids (2ry ligand) are reported. Cu(II) complexes were characterized on the bases of their elemental analyses, IR, ESR and thermal analyses. The elemental analysis indicated the formation of mixed ligand complexes in a mole ratio 1:1:1 (Cu:L^1:L^2), L^1 = PBI and L^2 = oxalic acid, phthalic acid or malonic acid. IR spectra showed that PBI acts as a neutral bidentate coordinated to the Cu(II) via the pyridyl and imidazolyl nitrogen atoms. The dicarboxylic acids are bidentate with monodentate carboxylate groups. Thermal decomposition study of complexes was monitored by thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis in N_2 atmosphere. The decomposition course and steps were analysed and the activation parameters of the nonisothermal decomposition were calculated from the TG curves and discussed. The isolated metal chelates were screened for their antimicrobial activities and the results are reported, discussed and compared with some known antibiotics.

Keywords: 2-(2-Pyridyl)-benzimidazole; Dicarboxylic acids; Complexes; IR; ESR; Thermal decomposition; Biological activity

1. Introduction

Metal complexes of biologically important ligands are sometimes more effective than free ligands [1]. Mixed ligand complexes have a key role in biological chemistry [2] because the mixed chelation occurs commonly in biological fluids as millions of potential ligands are likely to compete for metal ions in vivo [3]. These create specific structures [2–4] and have been implicated in the storage and transport of active substances through membranes. Among these ligands are benzimidazole and its derivatives where transition metal complexes with benzimidazoles are progressively used to model important bioinorganic systems [5]. For example, the antiviral activity of some 2-substituted benzimidazole derivatives considered to be related to their ability to chelate trace metal ions in biological systems [6]. Furtheremore benzimidazole complexes exhibit a broad spectrum of biological activities including antifungal [7,8], antibacterial [9,10], antimicrobial [11,12], antiamobeic [13,14], antiparasitic [15] and antitumor [16,17]. As a part of research on metal complexes with benzimidazole derivatives and carboxylate ligands [18,19], we aim to synthesize and characterize copper(II) complexes with 2-(2-pyridyl)-benzimidazole (**I**), and aliphatic or aromatic dicarboxylic acids. The study also includes thermal analysis and biological activity of the synthesized complexes.



2-(2-pyridyl)-benzimidazole (PBI).

(I)

Abbreviations: PBI, 2-(2-pyridyl)-benzimidazole; ox, oxalic acid; mal, malonic acid; phth, phthalic acid

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2. Experimental

2.1. Materials and physical measurements

$CuCl_2{\cdot}2H_2O$ was supplied from BDH. 2-(2-Pyridyl)-benzimidazole (PBI) was obtained from Aldrich Chem. Co. The dicarboxylic acids: oxalic acid·$2H_2O$ (ox), malonic acid (mal) and phthalic acid (phth) were provided by Sigma Chem. Co. The microchemical analysis of the separated solid complexes for C, H and N were performed in the Centeral Microanalytical Laboratory, Chemistry Department, Cairo University, Egypt. The analyses were performed twice to check the accuracy of the analyses data. Infrared spectra were recoreded on a 8001-PC FTIR Shimadzu spectrophotometer using KBr pellets. Measurement was performed by using a dynamic nitrogen atmosphere with a TGA-50 Shimadzu thermogravimetric analyzer at a flow rate of 20 mL min^{-1}. The heating rate was 10 °C min^{-1} in the temperature range 30–1000 °C using platinum crucibles and the sample sizes ranged in mass from 6 to 8 mg. The activation parameters of the thermal events were calculated by Coats and Redfern's method [20].

2.2. Synthesis

The copper(II) complexes were synthesized according to the general method viz.: 2-(2-pyridyl)-benzimidazole (0.001 mol; 0.1952 g), dicarboxylic acid (0.001 mol; 0.126, 0.104, 0.166 g of oxalic, malonic and phthalic acid, respectively) and $CuCl_2{\cdot}2H_2O$ (0.001 mol; 0.1705 g) were dissolved in ethanol–water mixture, 1:1 (v/v) (50 mL). To this mixture, a solid $NaHCO_3$ (0.002 mol; 0.168 g) was added portionwise. After complete addition of the bicarbonate, the reaction mixture was stirred for 2 h at room temperature. The solid precipitated was collected by filtration, washed several times with EtOH, followed by Et_2O and dried under vacuum over silica gel. The analytical data were given in Table 1.

2.3. Biological activity

A 0.5 mL spore suspension (10^{-6} to 10^{-7} spore mL^{-1}) of each of the investigated micro-organisms was added to a sterile agar medium just before solidification, then poured into sterile petri dishes (9 cm in diameter) and left to solidify. By using a sterilized cork borer (6 mm in diameter), three holes (wells) were made in each dish, then 0.1 ml of the tested compounds dissolved in DMSO (100 μg mL^{-1}) were poured into these holes. Finally, the dishes were incubated at 37 °C for 48 h where clear or inhibition zones were detected around each hole. 0.1 mL DMSO alone was used as a control under the same conditions for each organism and by subtracting the diameter of inhibition zone resulting with DMSO from the obtained in each case, both antibacterial activities can be calculated as a mean of three replicates.

Three different concentrations (1, 2.5 and 5 mg mL^{-1}) of the test compounds were screened against Gram positive and Gram negative bacteria in DMSO to evaluate the effect of concentration of the compounds on the activity of the bacteria.

Table 1
Analytical data Cu(PBI)–L[a] complexes

Compound	M_{wt}	Found (calculated) (%)		
		C	H	N
[Cu(PBI)(ox)].H_2O	364.5	45.88(46.09)	2.96(3.01)	11.41(11.52)
[Cu(PBI)(mal)].H_2O	378.5	47.39(47.55)	3.35(3.43)	11.01(11.09)
[Cu(PBI)(Phth)]	422.5	56.23(56.80)	3.11(3.07)	9.84(9.94)

[a] L: oxalic acid (ox); malonic acid (mal); phthalic acid (phth).

3. Results and discussion

3.1. IR spectra and mode of bonding

In absence of a powerful technique such as X-ray crystallography, IR spectra has proven to be the most suitable technique to give enough information to elucidate the way of bonding of the ligands to the metal ions. The main IR bands with their tentative assignments are summarized in Table 2. The spectra of all complexes exhibit two bands in the 3092–3061 cm^{-1} region in the complexes can be attributed to the primary ligand NH stretching vibration. The new bands at 1648–1635 and 1416–1385 cm^{-1} in the spectra of all complexes are assigned to asymmetric and symmetric stretching vibrations of coordinated carboxylate group [21]. This assignment is based on the fact that the unionized and uncoordinated COO^- stretching band occurs at 1750–1700 cm^{-1} [21]. Decon showed that the magnitude of the $\Delta\nu = \nu_{asy}(COO^-) - \nu_{sym}(COO^-)$ can be used to distinguish between the different coordination modes of the ligands either monodentate or bidentate[22]. This difference is found to be 289–313 cm^{-1} reflecting the monodentate coordination of each carboxylate group in the synthesized complexes. Therefore, the dicarboxylic acids act as bidentate coordinated to the copper(II) centers via two monodentate carboxylate groups. In some complexes a band at 1573–1551 cm^{-1} can be attributed to the $\nu_{C=N}$. The spectra of the complexes display the in-plane ring deformation bands of the pyridine moiety, Table 2, at 760–753, 633–630 and 583–580 cm^{-1} which are higher than the free pyridine ring suggesting the coordination of the pyridyl nitrogen to the copper(II) ion.

Table 2
Tentative assignment of the important infrared bands of the synthesized ternary complexes Cu(PBI)–L complexes

Complex	υ_{NH}	$\upsilon_{C=N}$	$\upsilon_{C=C}$	υ_{COO} (symmetry)	υ_{COO} (asymmetry)	$\Delta\upsilon$	$\delta_{(py)}$
PBI	3061, 3080	1600	1445	–	–	–	620, 590, 547
[Cu(PBI)(ox)]·H_2O	3061, 3087	1573	1459	1344	1635	291	760, 633, 583
[Cu(PBI)(mal)]·H_2O	3062, 3090	1560	1452	1331	1644	313	740, 630, 582
[Cu(PBI)(Phth)]	3067, 3092	1551	1456	1359	1648	289	753, 632, 580

Table 3
Electron spin resonance data of Cu(PBI)–L complexes

Compound	$g_{\|\|}$	$g_{\perp}$	g_{avg}	G
[Cu(PBI)(ox)]·H_2O	2.208	2.062	2.111	3.41
[Cu(PBI)(mal)]·H_2O	2.238	2.091	2.140	2.65
[Cu(PBI)(Phth)]	2.254	2.075	2.135	3.42

3.2. Electron spin resonance study

The X-band ESR spectra of the isolated solid complexes recorded at room temperature are anisotropic and exhibit two "g" values. The $g_{||}$ and $g_{\perp}$ values are computed from the spectrum using DPPH free radical as "g" marker. The average g values were calculated according to the equation $g_{av} = (1/3)[g_{||} + 2g_{\perp}]$ and the results are given in Table 3. Kivelson and Neiman [23] have reported that $g_{||} < 2.3$ and $g_{||} > 2.3$ is characteristic for covalent and ionic characters, respectively. By applying this criterion, the complexes under study have mainly covalent metal–ligand bonding. The trend $g_{||} > g_{\perp} > g_e(2.0023)$ observed for these complexes shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu(II) ion [24,25]. In addition the exchange coupling interaction between two copper centers in solid state given by Hathway [26,27] expression, $G = (g_{||} - 2.0023)/(g_{\perp} - 2.0023)$, led to the values of 2.65–3.42, Table 3. According to Hathway, if the value of G is greater than four, the exchange interaction is negligible, whereas when the value of G is less than four a considerable interaction is indicated in solid complexes. Accordingly there is a considerable exchange interaction between the copper centers in the solid state. Based on elemental analysis, IR and ESR data, a tetragonally distorted copper(II) complexes is assumed for all isolated complexes.

3.3. Thermal analysis

The thermogravimetric (TG) and the derivative thermogravimetric (DTG) plots of complexes are given in Fig. 1. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formulae of the complexes. The temperature range, the predicted intermediates and final products are given in Table 4.

3.3.1. [Cu(PBI)(ox)]·H_2O

The TG and DTG Curves of [Cu(PBI)(ox)].H_2O are shown in Fig. 1a. The thermogram exhibits three main distinct decomposition steps. The first step of decomposition within the temperature range (50–140 °C) corresponds to the loss of water molecule of hydration with a mass loss 4.7% (calculated 4.9%). The second step (209–323 °C) corresponds to the loss of oxalic anhydride molecule(C_2O_3) with mass loss 18.6% (calculated 19.75%). The third step (407–551 °C) corresponds to the loss of PBI molecule with mass loss 54.5% (calculated 53.5%). The energies of activation were 22.4, 35.0 and 47.1 kJ mol^{-1} for the first, second and third steps, respectively. The total mass loss up to 551 °C is in agreement with the formation of CuO as the final residue (TG 22.2%, calculated 21.8%).

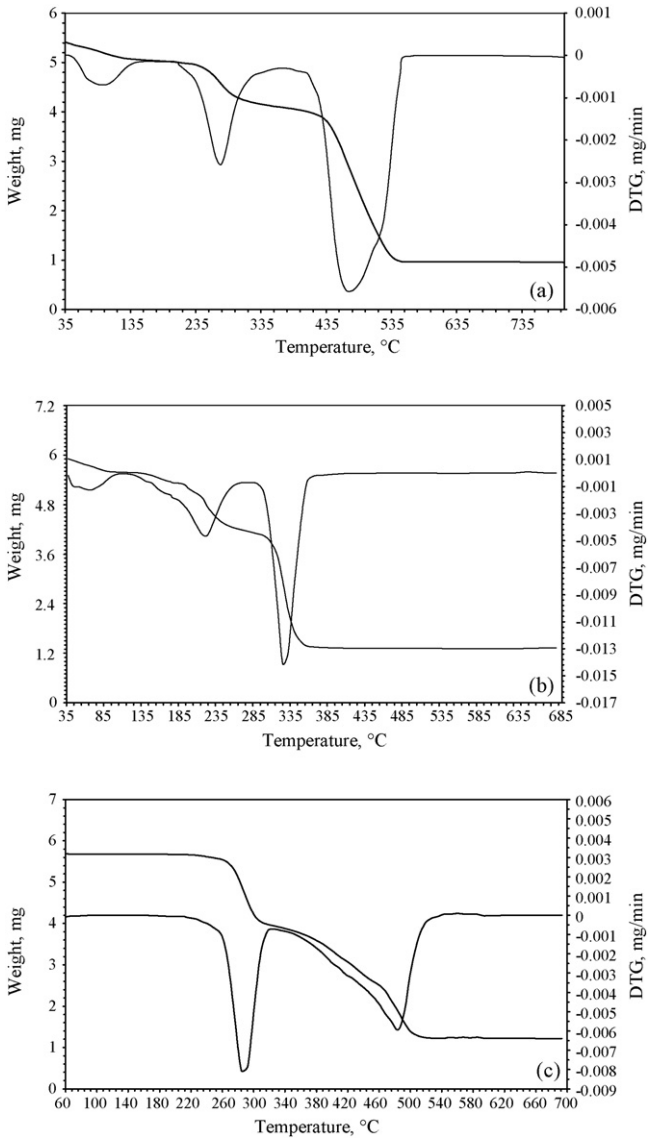

Fig. 1. TG and DTG plots of Cu-PBI-dicarboxylic acid complexes. Curves: (a) [Cu(PBI)(ox)]; (b) [Cu(PBI)(mal)]; (c) [Cu(PBI)(phth)].

3.3.2. [Cu(PBI)(mal)]·H_2O

The Thermogram given in Fig. 1b of [Cu(PBI)(mal)]·H_2O exhibits three significant thermal events within the temperature range (37–366 °C). The first step of decomposition within the temperature range (37–100 °C) corresponds to the loss of water molecule of hydration with a mass loss 4.5% (calculated 4.7%). The second step (125–224 °C) corresponds to the loss of malonic anhydride ($C_3H_2O_3$) with mass loss 22.5% (calculated 22.7%). The third step (291–366 °C) corresponds to the loss PBI molecule with mass loss 50.9% (calculated 51.5%). The energies of activation were 31.6, 16.7 and 64.4 kJ mol^{-1} for the first, second and third steps, respectively. The total mass loss up to 366 °C is in agreement with the formation of CuO as the final residue (TG 22.1%, calculated 21.1%).

Table 4
Stepwise thermal degradation data obtained from TGA curves for Cu(PBI)–L complexes

Complex	Molar mass	TG range (°C)	DTG_{max}	Weight loss		Assignment	Metallic residue found (calculated %)
				Found	Calculated		
[Cu(PBI)(ox)]·H_2O	364.5	50–140	91	4.7	4.9	Loss of H_2O	CuO 22.2 (21.8)
		209–323	274	18.60	19.75	Loss of oxalic anhydride	
		407–551	474	54.5	53.5	Loss of PBI	
[Cu(PBI)(mal)]·H_2O	378.5	37–100	68	4.5	4.7	Loss of H_2O	CuO 22.1 (21.1)
		125–224	224	22.5	22.7	Loss of malonic anhydride	
		291–366	325	50.9	51.5	Loss of PBI	
[Cu(PBI)(Phth)]	422.5	226–325	284	34.8	35.0	Loss of phthalic anhydride	CuO 19.5(18.8)
		351–526	484	45.7	46.1	Loss of PBI	

3.3.3. *[Cu(PBI)(Phth)]*

The TG and DTG curves of [Cu(PBI)(phth)] are shown in Fig. 1c. The TGA curve of the Cu(PBI)(phthalate) complex shows two stages of decomposition within the temperature range (226–526 °C). The first step of decomposition within the temperature range (226–325 °C) corresponds to the loss phthalic anhydride molecule with a mass loss 34.8% (calculated 35.0%). The second step (351–526 °C) corresponds to the loss of PBI with mass loss 45.7% (calculated 46.1%). The energies of activation were 102.3 and 9.8 kJ mol^{-1} for the first and second steps, respectively. The total mass loss up to 526 °C is in agreement with the formation of CuO as a final residue (TG 19.5%, calculated18.8%).

3.4. Kinetic data of the decomposition of complexes

The thermodynamic activation parameters of decomposition processes of complexes namely activation energy (E_a), enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free energy change of the decomposition (ΔG^*) were evaluated graphically by employing the Coats–Redfern relation method [20]. This method, as reviewed by Johnson and Gallagher [28] is an integral method that assumes various orders of reaction and compares the linearity in each case to select the correct order. The equations are given below:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\left[\frac{AR}{\theta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.303RT}, \quad \text{for } n \neq 1 \tag{1}$$

$$\log\left\{\frac{-\log(1-\alpha)}{T^2}\right\} = \log\left[\frac{AR}{\theta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.303RT}, \quad \text{for } n = 1 \tag{2}$$

where α is the fraction of sample decomposed at time t, T the derivative peak temperature, A the frequency factor, E_a the activation energy, R the gas constant, θ is the heating rate and $(1-(2RT/E_a)) \cong 1$. A plot of $\log\{-\log(1-\alpha)/T^2\}$ versus $1/T$ gives a slope from which the E_a is calculated and A (Arrhenius factor) is determined from the intercept. The entropy of activation was calculated using Eq. (15) [29].

$$\Delta S^* = 2.303R\left[\log\left(\frac{Ah}{kT}\right)\right] \tag{15}$$

where h and k stand for the Planck and Boltzmann constants, respectively and T is the Peak temperature from the DTG curve. The free energy of activation ΔG^* and the enthalpy of activation ΔH^* were calculated using Eqs. (3) and (4), respectively.

$$\Delta H^* = E_a - RT \tag{3}$$

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \tag{4}$$

The left-hand side of Eqs. (1) and (2) is plotted and in testing the thermal decomposition data of complexes, Eqs. (1) and (2) expressing the integer and non-integer orders were plotted. The first order equation is found to be better. The kinetic data obtained from the nonisothermal decomposition of the complexes are cited in Table 5. According to the kinetic data obtained from DTG curves, all the complexes have negative entropy, indicating that the activated complexes are more ordered than the reactants.

3.5. Antibacterial activity

The biological activity of the isolated mixed ligand complexes and Chloroamphenicol (as a standard compound) were tested against bacteria because bacteriums can achieve resistance to antibiotics through biochemical and morphological modifications [30]. In testing the antibacterial activity of these compounds, we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The organisms used in the present investigations included two Gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtillis* and two Gram negative bacteria (*Pseudomonas aereuginosa* and *Escherichia coli*). The diffusion agar technique was used for screening the antibacterial activity of the synthesized mixed ligand complexes [31–34]. The medium used for growing the culture was nutrient agar. The results of the bactericidal screening of the synthesized compounds are recorded in Table 6. The data obtained reflect the following results:

1. Antibacterial activity of all mixed ligand complexes towards *E. coli* are detected; except [Cu(PBI)(ox)] complex.

Table 5
The kinetic parameters for the non-isothermal decomposition of the Cu(PBI)–L complexes

Range (°C)	T^a	E_a (kJ mol^{-1})	A (S^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
[Cu(PBI)(ox)]·H_2O						
50–140	91	22.45	1.43	19.42	−243.9	108.2
209–323	274	35.01	4.0E−01	30.45	−257.9	171.5
407–551	474	47.06	1.6E−01	40.85	−268.1	241.1
[Cu(PBI)(mal)]·H_2O						
32–77	48	31.59	4.34E+01	28.76	−215.08	102.1
171–250	234	16.67	1.9E−03	12.54	−301.6	162.4
321–408	375	64.35	1.4E+02	59.38	−210.01	184.9
[Cu(PBI)(phth)]						
226–325	284	102.3	2.27E+06	97.71	−128.8	169.5
351–526	484	9.79	7.12E−05	3.50	−332.4	255.1

[a] The peak temperature from the DTG curve.

Table 6
Antibacterial activity of the isolated mixed ligand Cu(PBI)–L complexes

Complex	Gram positive						Gram negative					
	Staphylococcus aureus			*Bacillus subtillis*			*Pseudomonas aereuginosa*			*Escherichia coli*		
	1[a]	2.5[a]	5[a]	1	2.5	5	1	2.5	5	1	2.5	5
1	++	++	+++	+	++	+++	+	++	+++	−	+	++
2	+	++	+++	+	++	+++	−	+	++	+	++	+++
3	−	++	+++	++	++	+++	+	++	+++	+	++	+++
Chloroamphenicol (standard)		++	++	++	+++	+++	++	+++	+++	++	++	++
Amikain			R						+++			
Augmantin			+++						R			
Unasyn			+++						R			
Septrin			R						R			
Cefobid			R						R			
Ampicillin			R						++			
Erythrpmycin			+++						R			

The test was done using the diffusion agar technique. (−) Non-detected, inhibition values = 0.7–0.9 cm beyond control; (+) less active, inhibition values = 1–1.5 cm, beyond control; (++) moderate active, inhibition values > 1.5 cm, beyond control; (+++) highly active. (1) [Cu(PBI)(ox)]; (2) [Cu(PBI)(mal)]; (3) [Cu(PBI)(phth)].
[a] Concentration (mg ml^{-1}).

2. The two complexes [Cu(PBI)(phth)] and [Cu(PBI)(ox)] have moderate activity towards *P. aereuginosa* and high activity towards *B. subtillis* and *S. aureus*.
3. The activity of the isolated complexes increases as the concentration increases because it is a well-known fact that concentration plays a vital role in increasing the degree of inhibition [35].
4. The data in Table 6 shows that E. coli was inhibited by the isolated complexes according to this order [Cu(PBI)(phth)] > [Cu(PBI)(mal)] > [Cu(PBI)(ox)] complexes. The importance of this lies in the fact that these complexes could be applied fairly in the treatment of some common diseases caused by *E. coli*, e.g. septicaemia, gastroenteritis, urinary tract infections and hospital acquired infections [36,37].
5. Furtheremore, some known antibiotics are tested toward *S. aureus* (as Gram positive) and *P. aereuginosa* (as Gram negative). The selected antibiotics are Amikain, Augmantin, Unasyn, Septrin, Cefobid, Ampicillin and Erythromycin. The given data in Table 6 show that Amikain, Augmantin, Unasyn, Septrin, Cefobid and Ampicillin have resistance effect toward *S. aureus* in contrast to the synthesized mixed ligand complexes. However, Augmantin, Unasyn, Septrin, Cefobid and Erythromycin, have resistance effect toward *P. aereuginosa* while all synthesized mixed ligand complexes have a greater effect. [Cu(PBI)(mal)] show moderate activity toward *Pseudomonas aereuginosa* similar to that of Ampicillin antibiotic.

4. Conclusion

The synthetic procedure in this work resulted in the formation of complexes in the molar ratio (1:1:1) (M:L^1:L^2), respectively. In these complexes the 1ry ligand (PBI) coordinated to Cu(II) metal ion through the two nitrogen atoms of imidazole and pyridine rings while the dicarboxylic acids are coordinated via the two oxygen atoms of carboxylate groups. From elemental analysis, IR and ESR all complexes having a tetragonal distorted structure with covalent metal–ligand bonding. Also these complexes show antibacterial activity, so synthesis of such complexes might be recommended.

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