Aziz and Yousif *Iraqi Journal of Science, 2022, Vol. 63, No. 7, pp: 2804-2813*
DOI: 10.24996/ijs.2022.63.7.5

ISSN: 0067-2904

Characterization Studies on Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes with New Ligands Derived from Anthraquinone Substance

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Received: 11/8/2021 Accepted: 17/11/2021 Published: 30/7/2022

Abstract

This work involves preparation of new metal complexes *via* reaction of two anthraquinone ligands with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions . The ligands are prepared by treatment of 1- and 2-anthraquinone with acetic anhydride.

The complexes are characterized by different physicochemical methods; microelemental analysis, molar conductivity, FT-IR, UV-Vis spectra and magnetic measurements. The discussion of the outcome data of the prepared complexes indicates that all complexes are octahedral.

The biological activity properties of the ligands and most of their complexes are studied using gram-positive and gram-negative bacteria, which indicate that only two of the complexes show biological activity.

Keywords: Anthraquinone, Metal ions, Acetic anhydride, Biological activity

دراسات تشخيصية لعدد من معقدات Mn(II)، Co(II)، Cu(II)، Ni(II)، Zn(II) و Cd(II) مع ليكاندات جديدة مشتقة من مادة الانثراكوينون

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الخلاصة

هذا العمل يتضمن تحضير معقدات فلزية جديدة عن طريق تفاعل اثنين من ليكاندات الانثراكوينون مع الايونات الفلزية{(Mn (II) Co(II), Cd(II), Zn(II) Cu(II)} Ni(II)}. اللكيندات حضرت بمعاملة 1 و 2– انثراكوينون مع اسيتيك انهيدريد.

شخصت المعقدات بطرق فيزيائية وكيميائية من خلال التحليل الدقيق للعناصر و استخدام الموصلية الكهربائية المولارية والقياسات الطيفية (FT–IR,UV–vis) وقياسات العزم المغناطيسي واستنادا الى هذه القياسات فقد اقترح ان تراكيب المعقدات المحضرة تمتلك بنية ثمانية السطوح.

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درست الفعالية المضادة للبكتريا لمركبات الليكاندات واغلب المعقدات باستخدام نوعين من البكتريا (الموجبة والسالبة لصبغة كرام) ووجد ان هناك معقدين فقط لهما فعالية بايولوجية.

1. Introduction

Anthraquinones represent an important part of organic compounds that can be produced synthetically in laboratories and many of its derivatives may be found in nature (bacteria and fungi) [1-3]

Athraquinone and its derivatives have many applications for example, in the textile industry [4,5], dyes, cosmetics, medicines, imaging devices [6,7], plastics and rubbers [8,9]. The derivatives of anthraquinone can produce many pharmacological activities, which include anti-inflammatory [10,11] and antifungal [12].

There are nearly a thousand compounds of anthraquinones that contain different types of compensator in different locations [13,14], which leads to a great diversity in the pharmacological effects of these compounds.

The presence of compensators such as the OH and CO groups in the cyclic structure of anthraquinone opens the possibility of forming a homogeneous group with metal ions [15].

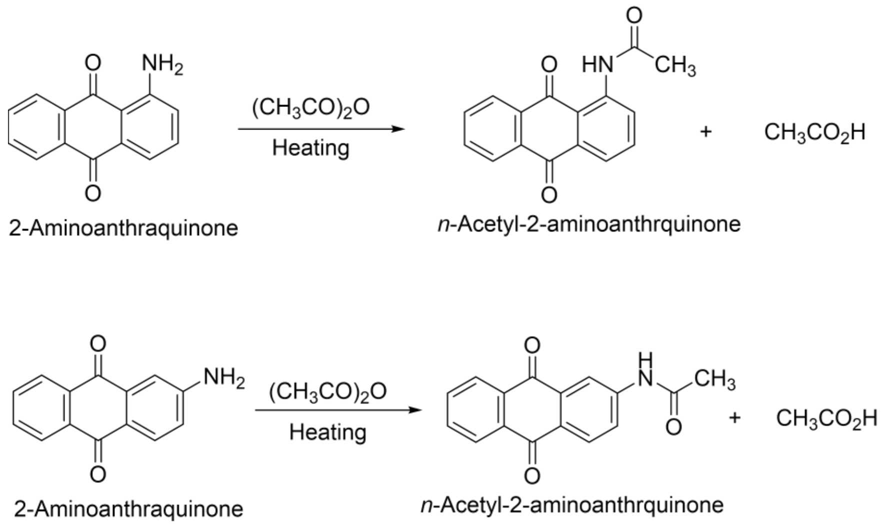
The constant interest in studying of the anthrquinone compounds lead researchers to consider the formation of metal complexes. Sharma, Tyagi and Ratnam [16] were prepared bis-(2-aminoanthraquinone) malonyldihydrazone and reacted with Mn(II), Ni(II)and Cu(II) from complexes of the type [$M_1L_1Cl_2M_2(L_2)_2$] where M_1=Cu(II),Ni(II), M_2=Cu(II), Mn(II), L_1=bis-(2-amino-anthrquinone) malonydihydrazone,L_2=5-nitrondazole.

In 2011, Jasim [17] has synthesized a number of new complexes *via* reaction of Mn(II), Co(II), Ni(II) and Cu(II) metal ions with [α-methyl-*N*-(3-methylideneindol)-2-aminoanthraquinone] ligands in molar ratios 1:1 and 1:2 to give complexes in general forms [$MLCl_2$]and[$M(L)_2Cl_2$]. The electrical conductivity measurements indicate that the complexes were not electrically conductive, and the measurements of the electronic spectra and the magnetic moments showed that some of the complexes possessed a tetrahedral structure and the other octahedral structure. Yousif [18] has reported a reaction between 1-aminoanthraquinone and 2-acetyl furan to afford (1-(furan-2-yl) ethylideneamino) anthracene-9, 10-dione. This compound was taken with metallic elements Mn(II), Co(II), Cu(II), Zn(L2) and Cd(II) in molar ratios (1:1) and (1:2) to prepare new compounds of the types [$MLCl_2$] and [Ml_2Cl_2]. After taking measurements of the prepared complexes, it was found that some of these complexes possess a tetrahedral structure and the others are octahedral structure.

In our present study, the ligands were successfully synthesized by the reaction of 1-aminoanthrquinone and 2-aminoanthraquinone with the acetic anhydride. Following this, the complexes of these two prepared ligands with six metals {Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)} were studied and characterized.

Preparation of ligands

The ligands *n*-acetyl-1-aminoanthrquinone and *n*-acetyl-2-aminoanthrquinone were prepared according to the literature procedure [19]. This was done by warming 1 or 2-aminoanthraquinone with an excess of acetic anhydride (Scheme 1) before pouring the mixture to water. The solid formed was filtered off, washed well with water and recrystallized twice from acetone and concentrated in *vacuo*. The melting point of the product is 253-255 °C. The ligand *n*-acetyl-2-aminoanthraquinone was prepared using similar procedure to that used for 2-aminoanthraquinone. The melting point of the product is 292-295 °C.



Scheme 1: Synthesis of the ligands

2. Experimental part

Preparation of metal complexes

A solution of the appropriate manganese chloride(II) salt (1 mmol) in a minimum volume of methanol was added to a solution of *n*-acetyl-1 and 2-aminoanthrquinone (2 mmol). The mixture was then warmed and stirred for 1 hour. The purple solid which deposited was filtered off and washed with acetone and light petroleum.

Similar procedure was used for the preparation of Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) complexes.

Biological activity:

Preliminary biological activity screening of the synthesized compounds has been performed in 100 µg/ml DMF against microorganism representing gram-positive bacteria (*Staphylococcus aureus*) and gram negative bacteria (*Escherichia coli*), using nutrient agar medium. By pouring the sterile agar into petri dishes in septic conditions, 100 µL of each standardized test organism culture was spread onto agar plates [20]. The sensitivity of microorganisms to antimicrobial agents was determined by the assay plates, which were incubated at 37°C for 24 hours.

Physical measurements:

All measurements have been done at room temperature, and the molar conductivity of the complexes was measured using DMSO with a conductivity meter PMC$_3$ (JENWAY). The measurements were carried out at a concentration of 10^{-3} M. The FT-IR spectra measurements of the ligands with complexes were measured using a spectrophotometer Bruker (Tensor27), in the range 200-4000cm^{-1}. A Shimadzu spectrophotometer with quartz cells was used to measure the UV-visible. The magnetic measurements of the complexes were measured by Faraday method using BRUKER BM6 type.

The complexes of Ni(II), Cu(II) and Zn(II) were analyzed using standard solutions of EDTA and suitable indicator [21. Also, a spectroscopic method was used to estimate cobalt using a UV-visible spectroscopy [22]. The chloride in the complexes was determined using ~~the~~ Mohr method [21].

Finally, C.H.N microanalysis of the ligands and the prepared complexes were analyzed at the laboratories of Ordu University, Ordu, Turkey.

3. Results and discussion

Table 1 displays the electrical conductivity values in DMSO solvent for the all complexes. It is noticed that some of the complexes are non-conductive, others are conductive in the ratio

1:1 [19,23]. Complexes of the general formula [$M(L)_2Cl_2$] where (M = Cu, Zn = Cd) and (L = A_1, A_2) are non-conductive. While, the complexes of the formula [$M(L)_2Cl.H_2O$]$Cl.H_2O$ where (M = Mn, Co, Ni) and (L = A_1, A_2) are conductive [19].

Table 1- Physical and analytical data for the ligands and their complexes

No.	**Compounds**	**Color**	**m. p. (°C)**	**Yield (%)**	**Λ_m cm^2.ohm^{-1}. mol^{-1}**	**M% Found (calc.)%**	**Cl% Found (calc.)%**	**Found (calc.)%**		
								C	**H**	**N**
L1	$C_{16}H_{11}N_1O_3$	Dark red	253-255	86.4				72.95 (72.45)	4.08 (4.15)	5.95 (5.28)
L2	$C_{16}H_{11}N_1O_3$	Dark red	292-295	82.4				71.98 (72.45)	4.20 (4.15)	5.51 (5.28)
1	[$M_n(L_1)_2Cl-H_2O$]$Cl.H_2O$	Maroon purple	223-225	77.02	42.4	-----	10.75 (10.262)	55.35 (55.66)	3.31 (2.89)	3.93 (4.05)
2	[$Co(L_1)_2Cl.H_2O$]$Cl.H_2O$	Dark green	272-275d	72.9	52.1	7.8 (8.46)	9.8 (10.20)	55.21 (55.34)	3.34 (2.88)	4.05 (4.03)
3	[$Ni(L_1)_2Cl.H_2O$]$Cl.H_2O$	Reddish brown	216-218	78.4	52.8	9.2 (8.4)	10.55 (10.207)	55.12 (55.36)	3.15 (2.88)	3.95 (4.03)
4	[$Cu(L_1)_2Cl_2$]	Maroon	107-110	88.3	22.7	8.8 (9.5)	10.39 (10.686)	57.81 (57.96)	3.00 (3.01)	4.12 (4.22)
5	[$Zn(L_1)_2Cl_2$]	Light orange	197-200	75.0	5.3	6.18 (5.3)	10.8 (10.66)	57.44 (57.80)	2.95 (3.01)	3.95 (4.21)
6	[$Cd(L_1)_2Cl_2$]	Reddish brown	268-270	86.7	12.5		10.86 (9.953)	53.64 (53.98)	2.50 (2.81)	3.81 (3.93)
7	[$Mn(L_2)_2Cl.H_2O$] $Cl.H_2O$	Green-brown	236-238	72.9	34.5	-----	(10.34) (10.262)	55.85 (55.66)	3.35 (2.89)	4.12 (4.05)
8	[$Co(L_2)_2Cl.H_2O$] $Cl.H_2O$	Dark green	187-190	85.5	47.4	7.9 (8.46)	9.7 (10.20)	54.98 (55.34)	3.12 (2.88)	4.15 (4.03)
9	[$Ni(L_2)_2Cl.H_2O$]$Cl.H_2O$	Maroon	548-250d	68.9	58.1	7.9 (8.4)	10.52 (10.207	55.41 (55.36)	3.39 (2.88)	3.99 (4.03)
10	[$Cu(L_2)_2Cl_2$]	Dark green	127-130	77.0	17.5	10.07 (9.5)	10.39 (10.686)	57.59 (57.96)	2.98 (3.01)	4.35 (4.22)
11	[$Zn(L_2)_2Cl_2$]	Red Brown	263-265	89.5	8.2	6.49 (5.3)	10.92 (10.66)	57.55 (57.80)	3.11 (3.01)	4.22 (4.21)
12	[$Cd(L_2)_2Cl_2$]	Dark brown	317-320d	83.4	13.8		10.46 (9.953)	53.73 (53.98)	2.77 (2.81)	4.01 (3.93)

Table 2 shows the magnetic moment values and the electronic spectrum measurements. The magnetic moment values by means of measurement the number of individual electrons. They were determined to the metal ions (Mn, Co, Ni and Cu) [24-27]. The electronic spectrum was measured for Co, Ni and Cu complexes. The manganese complexes are not expected to exhibit d-d transition in the visible region, because they are orbital and spin forbidden [28]. While, Zn and Cd complexes do not have d-d transitions, because electron transitions in these metals do not occur in d-orbitals since it is saturated with electrons, and if they give peaks, they are likely to be the charge transfer spectra reason [29].

The electronic spectrum of the Co complexes was measured and showed absorption peaks in the region 21739-19305 cm^{-1} attributed to ν_3 indicating the transition ($^4T_1g_{(T)} \rightarrow {}^4T_1g_{(p)}$), and other absorption peaks with band arise 15673-146525 cm^{-1} dependent to ν_2 and indicate transition ($^4T_1g_{(F)} \rightarrow A_2g_{(F)}$). As for ν_1 peaks ($^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$) appeared in the region 10000-9323 cm^{-1}, and these values are in agreement with Co(II) complexes of hexagonal octahedral symmetry [30-31].

The electronic spectrum was measured for the nickel complexes and it was observed that gives three absorption peaks. First one in the region 27322-27173 cm^{-1} attributed to the ν_3, ($^3A_2g_{(F)} \rightarrow {}^3T_1g_{(P)}$). The second one in the region between 166554 and 1568302 cm^{-1} attributed to the ν_2 ($^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$). The third one belongs to the ν_1 ($^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$) and appears in absorptions ranging from 10345 to 9636 cm^{-1}. The adsorption band sites of Ni complexes are consistent with the octahedral hexagonal symmetric complexes with literatures [32,33].

The Cu complexes showed a wide absorption band in 14939-15833 cm^{-1}, and belong to the two or three from the following transitions and this is attributed to Jan-Teller distortion

$^2B_1g \longrightarrow {}^2A_1g(\nu_1)$
$^2B_1g \longrightarrow {}^2B_2g\ (\nu_2)$
$^2B_1g \longrightarrow {}^2Eg\ (\nu_3)$

These values indicate that the Cu complexes are octahedral complexes [34]. The FT-IR data of the two prepared ligands are shown in Table 3. The absorption band at 1685 cm^{-1} is belonging to the stretching vibration of the carbonyl group in the (*n*-acetyl-1-aminoanthraquinone) (L_1). While the absorption band at 1692 cm^{-1} is attributing to the stretching vibrations of the carbonyl group in the (*n*-acety-2-aminoanthraquinone) (L_2) [35]. The stretching vibrations of the N-H group in the two ligands L_1 and L_2 appear at 3242 and 3247 cm^{-1}, respectively [19]. The stretching vibrations of the carbonyl group in the prepared complexes are shifted towards a lower frequency. In the first ligand (L_1) complexes, the displacement is about 30-35 cm^{-1}, and in the second ligand (L_1) complexes is between 32 and 37 cm^{-1} [35-37].

Table 2 - Electronic spectra (in DMSO) and magnetic moment.

No.	**Compounds**	**d-d. transition (cm^{-1})**			**M_{eff} (B.M)**
		ν_1	**ν_2**	**ν_3**	
1.	$[Mn(L_1)_2Cl.H_2O]Cl.H_2O$	-----	----	---	5.95
2.	$[Co(L_1)_2Cl.H_2O]Cl.H_2O$	9,328	15,673	21,739	4.82
3.	$[Ni(L_1)_2Cl.H_2O]Cl.H_2O$	9,363	15,683	27,322	3.25
4.	$[Cu(L_1)Cl_2]$	15,833	----	---	1.78
7.	$[Mn(L_2)_2Cl.H_2O]Cl.H_2O$	----	----	---	5.8
8.	$[Co(L_2)_2Cl.H_2O]Cl.H_2O$	10,000	14,652	19,305	4.74
9.	$[Ni(L_2)_2Cl.H_2O]Cl.H_2O$	10,345	16.655	27,173	3.3
10.	$[Cu(L_2)_2Cl_2]$	14,939	----	---	1.71

Table 3 - FT-IR frequencies (cm^{-1}) of the ligands and complexes

No.	Compound	ν(C=O) ring	ν(N-H)	ν(M-O)	ν(M-NH)	ν(M-Cl)
	L_1	1685	3242			
	L_2	1692	3247			
1.	$[Mn(L_1)_2Cl.H_2O]Cl.H_2\ O$	1655	3185	448	390	330
2.	$[Co(L_1)_2Cl.H_2O]Cl.H_2\ O$	1650	3173	445	380	345
3.	$[Ni(L_1)_2Cl.H_2\ O]Cl.H_2\ O$	1654	3197	447	360	335
4.	$[Cu(L_1)_2Cl_2]$	1651	3183	469	385	340
5.	$[Zn(L_1)_2.Cl_2]$	1655	3175	481	365	330
6.	$[Cd(L_1)_2Cl_2]$	1655	3180	444	370	335
7.	$[Mn(L_2)_2Cl.H_2\ O]Cl.H_2\ O$	1656	3185	475	390	340
8.	$[Co(L_2)_2Cl.H_2\ O]Cl.H_2\ O$	1657	3174	461	360	335
9.	$[Ni(L_2)_2Cl.H_2\ O]Cl.H_2\ O$	1658	3197	470	380	340
10.	$[Cu(L_2)_2Cl_2]$	1655	3183	476	390	330
11.	$[Zn(L_2)_2Cl_2]$	1659	3175	480	387	335
12.	$[Cd(L_2)_2Cl_2]$	1660	3180	481	385	335

Table 4- Stretching vibration rocking and wagging of the aqua complexes

No.	Compound	rocking (H_2O) Pr (H_2O)	wagging (H_2O) Pw (H_2O)	$M-OH_2$
1.	$[Mn(L_1)_2Cl.H_2O]Cl.H_2O$	794	653	405
2.	$[Co(L_1)_2Cl.H_2O]Cl.H_2O$	795	645	428
3.	$[Ni(L_1)_2Cl.H_2O]Cl.H_2O$	794	647	426
7.	$[Mn(L_2)_2Cl.H_2O]Cl.H_2O$	765	649	422
8.	$[Co.(L_2)_2Cl.H_2O]Cl.H_2O$	797	650	428
9.	$[Ni(L_2)_2Cl.H_2O]Cl.H_2O$	770	646	428

The stretching vibrations of the N-H group in the prepared complexes are also shifted to a lower frequency (45-68 cm^{-1} in L_1) and (55-68 cm^{-1} in L_2) as shown in Table 3 [38]. Also, new absorption bands appeared in the prepared complexes, which belong to M-O, M-NH, M-X bonds in 444-481 cm^{-1}, 360-390 and 330-345 cm^{-1}, respectively [39-41].

The FT-IR spectra of Mn, Co and Ni are exhibited bands of H_2O at 765-797cm^{-1} belonging to the rocking vibrations, and 645-653 cm^{-1} returning to the wagging vibrations. In addition, the stretching of the $M-OH_2$ appears within limits 405-428 cm^{-1} as shown in Table 3 [42].
Finally, the absorption band of the carbonyl at acetyl group gave an absorption at 1718 cm^{-1} in L_1, and 1714 cm^{-1} in L_2 [19]. It was observed that this band did not shift when preparing the complexes, which indicates that the oxygen atom of the acetyl group is not bound with metal ions.

Biological activity

The biological activity of new anthraquinone complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) against *Staphylococcus aureus* (as gram positive) and *Escherichia coli* (as gram negative) using disk diffusion method [43,44].

The results showed that the complexes types $[Cd(L_1)_2Cl_2]$ and $[Cd(L_2)_2Cl_2]$ have higher antibacterial activities than others in gram-positive and gram-negative bacteria as shown in Table 5.

The Cd in complex types 6 and 12 may affect the function of some enzymes by binding to sulfhydryl groups then deactivating their protein structures in bacteria therefore showed higher biological activity in their complexes containing the cadmium metals.

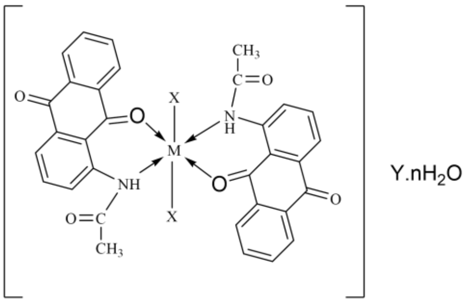
Table 5- Antibacterial activity of the ligand and its complexes

No.	Compound	***Staph.aureus***	***E.coli***
		Diameter of inhibition zone (mm)	**Diameter of inhibition zone (mm)**
L_1		R	R
L_2		R	R
1	$[Mn(L_1)_2Cl\text{-}H_2O]Cl.H_2O$	R	R
2	$[Co(L_1)_2Cl.H_2O]Cl.H_2O$	R	R
3	$[Ni(L_1)_2Cl.H_2O]Cl.H_2O$	R	R
4	$[Cu(L_1)_2Cl_2]$	R	R
5	$[Zn(L_1)_2Cl_2]$	R	R
6	$[Cd(L_1)_2Cl_2]$	9	11
7	$[Mn(L_2)_2Cl.H_2O]Cl.H_2O$	R	R
8	$[Co(L_2)_2Cl.H_2O]Cl.H_2O$	R	R
9	$[Ni(L_2)_2Cl.H_2O]Cl.H_2O$	R	R
10	$[Cu(L_2)_2Cl_2]$	R	R
11	$[Zn(L_2)_2Cl_2]$	R	R
12	$[Cd(L_2)_2Cl_2]$	10	12

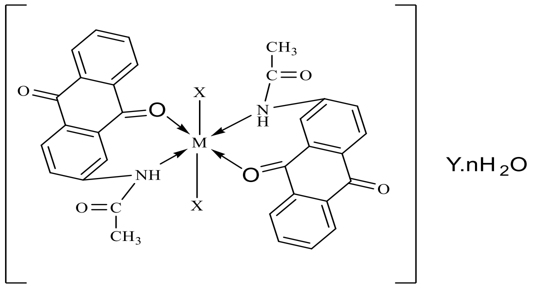
4. Conclusion

After characterizing and studying the prepared complexes, it was found that all the metals complexes are six coordinated octahedral complexes. The coordination of metals with the prepared ligands is done through the carbonyl group at anthraquinone ring and nitrogen atom of amide group as indicated by the measurements as the π type electronic density of the carbonyl group is shifted towards the metal ion on the other hand. The binding of amide nitrogen to the metals is attributed to the resulting weakness in the N-H, and thus the double nitrogen is given to the metal ion.

Based on the results of aforementioned physical measurements, the prepared complexes structures can be suggested as follows:



When M = Mn, Co, Ni
X = Cl, H_2O, Y = Cl; n = 1
When M = Cu, Zn, Cd
X = Cl; Y = 0, n = 0
With *n*-acetyl-1-aminoanthraquinone



When M = Mn, Co, Ni
X = Cl, H_2O, Y = Cl; n = 1
When M = Cu, Zn, Cd
X = Cl; Y = 0, n = 0
With *n*-acetyl-2-aminoanthraquinone

In this research, these complexes can be prepared for commercial use to prove their effectiveness against various diseases such as cancerous diseases.

Acknowledgements

We are grateful to all the staff in the College of Science / University of Mosul for their tremendous help.

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