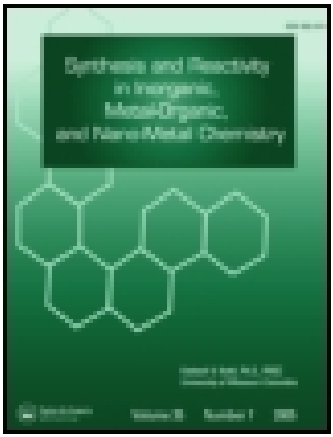

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Synthesis, Characterisation, Electrochemistry and Biological Activity of Ruthenium(III) Complexes Containing N.S Donor Ligands and Triphenylphosphine or Triphenylarsine

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SYNTHESIS, CHARACTERISATION, ELECTROCHEMISTRY AND BIOLOGICAL ACTIVITY OF RUTHENIUM(III) COMPLEXES CONTAINING N,S DONOR LIGANDS AND TRIPHENYLPHOSPHINE OR TRIPHENYLARSINE

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ABSTRACT

Several new hexa-coordinated low-spin d^5 ruthenium(III) complexes of the type $[RuX_2(TSC)(EPh_3)_2]$ (where X = Cl or Br; H-TSC = benzaldehyde thiosemicarbazone, cinnamaldehyde thiosemicarbazone, thiophene-2-carboxaldehyde thiosemicarbazone and 2-furaldehyde thiosemicarbazone, E = P or As) have been synthesised by the reactions of $[RuX_3(EPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ with the various thiosemicarbazones. All the new complexes were characterised using various physico-chemical methods such as elemental analysis, spectral (IR, UV-VIS, EPR), magnetic moment and cyclic voltammetry data. In all these complexes, the thiosemicarbazones are bonded to the central ruthenium ion through the thiolato sulphur, after

deprotonation, and the azomethine nitrogen. The antibacterial activity of some of the ligands and their complexes were also tested against two species of bacteria.

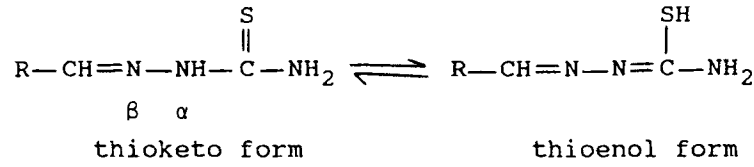
INTRODUCTION

One interest in the study of compounds containing sulphur and nitrogen is due to their significant antifungal, antibacterial and anticancer activity[1]. It is well known that some drugs have increased activity when administered as metal complexes than as free ligands[2-4]. Thiosemicarbazones and semicarbazones are a special class of azomethines[5] which act as ionic or neutral moieties having an interesting stereochemistry as only the β-nitrogen atom coordinates to the metal, while the α-nitrogen remains uncoordinated. On the other hand, the remaining sulphur or oxygen atoms form a strong covalent bond with the metal. Though a large number of reports are available on the chemistry and biocidal activity of thiosemicarbazone/semicarbazone complexes of transition metals, only very few reports on the ruthenium complexes are known[6,7]. In the present paper, we report the synthesis, characterisation, electrochemistry and antibacterial activity of some mixed ligand ruthenium(III) complexes containing thiosemicarbazones as one of the ligands.

The thiosemicarbazones used in the present study are of the type shown in Fig. 1.

EXPERIMENTAL

All reagents used were Analar grade. Solvents were were purified and dried before use according to standard



R = C_6H_5; H-BTSC (H-$C_8H_8N_3S$)

= $C_6H_5CH=CH$; H-CTSC (H-$C_{10}H_{10}N_3S$)

= 2-thiophene; H-TCTSC (H-$C_6H_7N_3S_2$)

= 2-furan ; H-FTSC (H-$C_6H_7N_3OS$)

Fig. 1. Structures of the Ligands

procedures. C, H, N analyses were perfomed at the R & D Laboratory, Hindustan Photo Film Industry, Udhagamandalam, India. Infrared spectra of the complexes were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometer in the 4000-250 cm^{-1} range. Electronic spectra of the complexes were recorded in dichloromethane with a Hitachi-Perkin Elmer 20/200 spectrophotometer. EPR spectra of the powdered samples were recorded on a Bruker ER-200D-SRC instrument at X-band frequencies, internally calibrated with diphenylpicrylhydrazyl (DPPH) and magnetic moments were measured on a EG & G-PARC vibrating sample magnetometer and diamagnetic corrections are applied. Melting points were determined using a Mettler FP 51 instrument and are uncorrected. The cyclic voltammetric studies were carried out in acetonitrile using a glassy carbon working electrode and all the potentials are referenced to a saturated calomel electrode (SCE).

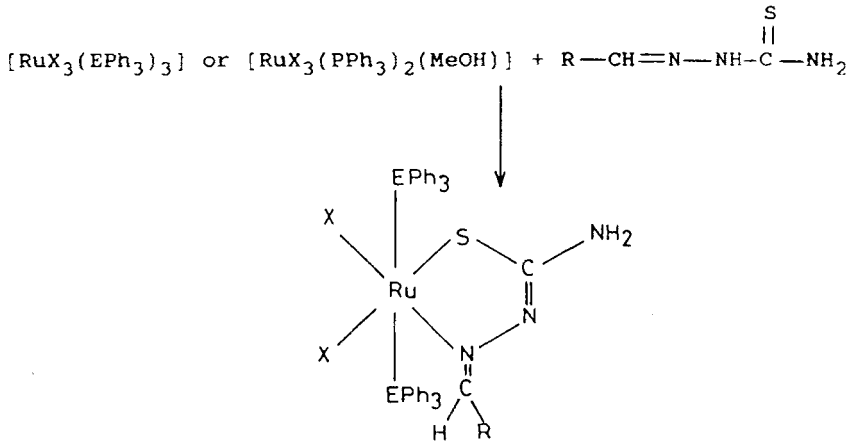
The starting complexes[8-11] $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, $[RuBr_3(PPh_3)_2(MeOH)]$ and $[RuBr_3(AsPh_3)_3]$ and the thiosemicarbazones[12-15] were prepared by the literature methods.

Preparation of the Complexes of the Type $[RuX_2(TSC)(EPh_3)_2]$ (X = Cl or Br; E = P or As; H-TSC = Various Thiosemicarbazones)

To a solution of $[RuX_3(EPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ (0.150 - 0.170 g, 0.125 mmol) in dry benzene (15 mL), a solution of the respective thiosemicarbazone (0.023-0.033 g, 0.125 mmol) in hot ethanol (5 mL) was added (molar ratio Ru complex : ligand ; 1 : 1). The resulting mixture was refluxed on a water bath for 4 h. After concentrating the solution to about 2 mL the product was separated by the addition of a small quantity of petroleum ether (60-80°c). The complex was then filtered, washed with petroleum ether and recrystallised from CH_2Cl_2/pet. ether mixture the ratio of which is 20 : 80. Yield: 0.092 g.

RESULTS AND DISCUSSION

The air- and light-stable complexes of the formula $[RuX_2(TSC)(EPh_3)_2]$ (where X = Cl or Br; E = P or As; TSC = thiosemicarbazones of various aldehydes) were synthesised by the reactions of $[RuX_3(EPh_3)_3]$ or $[RuX_3(PPh_3)_2(MeOH)]$ with the appropriate thiosemicarbazones in 1:1 molar ratio as shown by the equation below.



(X = Cl or Br; E = P or As; R = C_6H_5, $C_6H_5CH=CH$, 2-thiophene or 2-furan).

All the new complexes are soluble in benzene, chloroform, dichloromethane, DMSO and DMF. In all reactions, it has been observed that the thiosemicarbazone ligand behaves as a uninegative bidentate N,S-donor by substituting one of the tertiary phosphine, arsine or methanol groups and a halide ion from the starting complex to form a five-membered chelate ring[2]. The analytical data obtained for these complexes are in good agreement with the above molecular formula (Table I).

Infrared Spectra

The infrared spectra of the free ligands when compared with that of the new complexes confirm the coordination of thiosemicarbazones to the ruthenium metal. The infrared spectra of the free thiosemicarbazones display two bands around 3450 cm^{-1} and 3300 cm^{-1} which are assigned as due to

Table I. Analytical Data of Ru(III) Thiosemicarbazone Complexes

No.	Complex (empirical formula)	Colour	M.p. °C	Yield (%)	Analysis % Found (Calc.) Carbon	Hydrogen	Nitrogen
1.	$[RuCl_2(BTSC)(PPh_3)_2]$ $(C_{44}H_{38}N_3SP_2Cl_2Ru)(874.47)$	Brown	140	64	60.71 (60.42)	4.57 (4.35)	4.32 (4.80)
2.	$[RuCl_2(CTSC)(PPh_3)_2]$ $(C_{46}H_{40}N_3SP_2Cl_2Ru)(900.49)$	Yellow Brown	164[a]	60	61.64 (61.35)	4.71 (4.44)	4.92 (4.67)
3.	$[RuCl_2(TCTSC)(PPh_3)_2]$ $(C_{42}H_{37}N_3S_2P_2Cl_2Ru)(881.51)$	Brown	156	68	57.61 (57.22)	3.87 (4.19)	4.82 (4.76)
4.	$[RuCl_2(FTSC)(PPh_3)_2]$ $(C_{42}H_{37}N_3OSP_2Cl_2Ru)(865.45)$	Red Brown	192	60	57.91 (58.28)	4.53 (4.28)	5.12 (4.85)
5.	$[RuCl_2(BTSC)(AsPh_3)_2]$ $(C_{44}H_{38}N_3SAs_2Cl_2Ru)(962.81)$	Brown	154[a]	65	54.62 (54.91)	4.12 (3.95)	4.51 (4.36)
6.	$[RuCl_2(CTSC)(AsPh_3)_2]$ $(C_{46}H_{40}N_3SAs_2Cl_2Ru)(988.31)$	Red Brown	196	62	56.21 (55.89)	4.41 (4.05)	4.38 (4.25)
7.	$[RuCl_2(TCTSC)(AsPh_3)_2]$ $(C_{42}H_{37}N_3S_2As_2Cl_2Ru)(969.35)$	Brown	184	67	51.82 (52.04)	3.52 (3.82)	4.51 (4.33)
8.	$[RuCl_2(FTSC)(AsPh_3)_2]$ $(C_{42}H_{37}N_3OSAs_2Cl_2Ru)(953.29)$	Brown	125	61	52.62 (52.91)	3.41 (3.88)	4.71 (4.40)
9.	$[RuBr_2(BTSC)(PPh_3)_2]$ $(C_{44}H_{38}N_3SP_2Br_2Ru)(964.47)$	Brown	140	70	55.41 (55.73)	4.39 (4.01)	4.81 (4.43)
10.	$[RuBr_2(CTSC)(PPh_3)_2]$ $(C_{46}H_{40}N_3SP_2Br_2Ru)(989.23)$	Red Brown	124[a]	64	56.28 (56.74)	3.74 (4.10)	4.02 (4.31)

11.	$[RuBr_2(TCTSC)(PPh_3)_2]$ $(C_{42}H_{37}N_3S_2P_2Br_2Ru)(970.25)$	Yellow Brown	160	65	53.15 (52.84)	4.21 (3.86)	4.15 (4.39)
12.	$[RuBr_2(FTSC)(PPh_3)_2]$ $(C_{42}H_{37}N_3OSP_2Br_2Ru)(954.19)$	Brown	172	67	53.41 (53.77)	3.70 (3.95)	4.12 (4.47)
13.	$[RuBr_2(BTSC)(AsPh_3)_2]$ $(C_{44}H_{38}N_3SAs_2Br_2Ru)(1051.21)$	Brown	154[a]	62	50.61 (50.22)	3.98 (3.61)	4.28 (3.99)
14.	$[RuBr_2(CTSC)(AsPh_3)_2]$ $(C_{46}H_{40}N_3SAs_2Br_2Ru)(1077.23)$	Red Brown	162	64	51.64 (51.28)	3.97 (3.71)	3.47 (3.89)
15.	$[RuBr_2(TCTSC)(AsPh_3)_2]$ $(C_{42}H_{37}N_3S_2As_2Br_2Ru)(1058.23)$	Yellow Brown	192	60	48.04 (47.66)	3.87 (3.49)	3.65 (3.96)
16.	$[RuBr_2(FTSC)(AsPh_3)_2]$ $(C_{42}H_{37}N_3OSAs_2Br_2Ru)(1042.19)$	Brown	148	62	48.15 (48.40)	3.97 (3.55)	4.49 (4.02)

a - decomposition

ν_{as} and ν_{sym} of terminal NH_2 groups. These bands remain more or less unaltered in the spectra of the ruthenium complexes, indicating the non-involvement of this terminal NH_2 group in coordination. The absorption due to $\nu_{C=N}$ of the free thiosemicarbazones appeared in the 1600-1630 cm^{-1} region[16] and this band is shifted to lower wave numbers in the spectra of all the complexes, indicating the coordination of the azomethine nitrogen to the metal[17]. The absorption due to the secondary NH was found in the spectra of the free ligands around 3120-3200 cm^{-1} and this band disappeared in the spectra of the complexes which reveals the enolisation of the thione group before coordination. The $\nu_{C=S}$ band appearing around 820 cm^{-1} in the free ligands was shifted to around ~750 cm^{-1} which indicates a considerable change in bond order and a strong metal-sulphur bond[18-20] (Table II). Further, a medium intensity band at ~1080 cm^{-1} and due to ν_{C-N} or ν_{N-C-N}[21,22], is shifted to higher wave number on complexation. In addition to the above absorptions, bands due to triphenylphosphine, arsine and Ru-Cl/Br were also present in the spectra of all the complexes. From the IR spectral data it is inferred that the thiosemicarbazones are potentially uninegative bidentate ligands and the coordination sites are the β-nitrogen and the thiolato sulphur after deprotonation. The possibility of α-nitrogen coordination is ruled out because of considerable strain[5].

Electronic Spectra

The electronic spectra in Table II of all the complexes in dichloromethane showed two bands in the 360-265 nm region.

Table II. IR and Electronic Spectral Data of New Ru(III) Complexes

No.	Complex	ν C=N	ν N-C-N	ν C-S	λ_{max}(nm)
1.	$[RuCl_2(BTSC)(PPh_3)_2]$	1600	1090	760	320, 270
2.	$[RuCl_2(CTSC)(PPh_3)_2]$	1600	1090	740	320, -
3.	$[RuCl_2(TCTSC)(PPh_3)_2]$	1580	1100	750	345, 270
4.	$[RuCl_2(FTSC)(PPh_3)_2]$	1600	1090	750	350, 285
5.	$[RuCl_2(BTSC)(AsPh_3)_2]$	1590	1110	730	340, 290
6.	$[RuCl_2(CTSC)(AsPh_3)_2]$	1590	1100	740	360, 290
7.	$[RuCl_2(TCTSC)(AsPh_3)_2]$	1580	1110	750	350, 270
8.	$[RuCl_2(FTSC)(AsPh_3)_2]$	1600	1100	740	340, 265
9.	$[RuBr_2(BTSC)(PPh_3)_2]$	1600	1090	750	320, 280
10.	$[RuBr_2(CTSC)(PPh_3)_2]$	1590	1100	760	330, 280
11.	$[RuBr_2(TCTSC)(PPh_3)_2]$	1600	1100	750	340, 270
12.	$[RuBr_2(FTSC)(PPh_3)_2]$	1600	1110	740	- , 275
13.	$[RuBr_2(BTSC)(AsPh_3)_2]$	1590	1100	750	350, 280
14.	$[RuBr_2(CTSC)(AsPh_3)_2]$	1600	1100	760	340, 280
15.	$[RuBr_2(TCTSC)(AsPh_3)_2]$	1600	1110	750	325, 270
16.	$[RuBr_2(FTSC)(AsPh_3)_2]$	1600	1100	760	350, 285

In most of the ruthenium(III) complexes, the electronic spectra show only charge transfer transitions[23]. The extinction coefficients of the bands around 350 nm (ε , 2126-3480) are less than that of the bands around 280 nm (ε , 3170-4750). In general, the above values are higher than the one expected for a d-d transition. Hence, we assigned these bands as due to charge transfer transitions which are characteristics of Ru(III) octahedral complexes[6].

Magnetic Moment

The magnetic moments for the complexes $[RuCl_2(CTSC)(PPh_3)_2]$ and $[RuCl_2(TCTSC)(AsPh_3)_2]$ have been measured at room temperature. The values are found to be 1.68 BM and 1.72 BM, respectively, corresponding to one unpaired electron suggesting a low-spin t_{2g}^5 configuration for the ruthenium ion in an octahedral environment.

EPR Studies

The room temperature EPR spectra of powdered samples were recorded at X-band frequencies. All the spectra showed no indication of any hyperfine splitting. Most of the complexes exhibit spectra with $g_\perp$ around 2.16-2.31 and $g_{||}$ around 2.09-2.18 (Table III). For an octahedral field with tetragonal distortion $g_x = g_y \neq g_z$ and, hence, the two 'g' values indicate a tetragonal distortion in these complexes[24]. The presence of two 'g' values also indicate an axial symmetry for these complexes and, hence, the trans positions are assigned for triphenylphosphine, arsine groups[25,26]. The complexes $[RuCl_2(BTSC)(PPh_3)_2]$, $[RuCl_2(CTSC)(PPh_3)_2]$, and

Table III. EPR Spectral Data of Some Ru(III) Complexes

No.	Complex	g_1	g_2	g_3	$\langle g \rangle^*$
1.	$[RuCl_2(BTSC)(PPh_3)_2]$	-	2.16	-	2.16
2.	$[RuCl_2(CTSC)(PPh_3)_2]$	-	2.18	-	2.18
3.	$[RuCl_2(TCTSC)(PPh_3)_2]$	2.19	2.19	2.15	2.18
4.	$[RuCl_2(TCTSC)(AsPh_3)_2]$	2.27	2.27	2.15	2.22
5.	$[RuCl_2(FTSC)(AsPh_3)_2]$	2.31	2.31	2.18	2.27
6.	$[RuBr_2(CTSC)(PPh_3)_2]$	2.22	2.22	2.09	2.18
7.	$[RuBr_2(TCTSC)(AsPh_3)_2]$	2.27	2.27	2.12	2.22
8.	$[RuBr_2(FTSC)(AsPh_3)_2]$	-	2.17	-	2.17

$$\langle g \rangle^* = [\frac{1}{3} g_1^2 + \frac{1}{3} g_2^2 + \frac{1}{3} g_3^2]^{1/2}$$

$[RuBr_2(FTSC)(AsPh_3)_2]$ exhibit a single isotropic resonance with 'g' values in the range 2.16-2.18. Such isotropic lines are usually observed either due to the intermolecular spin exchange which can broaden the lines or due to the occupancy of the unpaired electron in a degenerate orbital. The average 'g' values are in the range 2.16-2.27 and the linewidths range from 50 to 170 Gauss. It has been observed that the nature and position of the lines in the EPR spectra of these complexes are similar to that of the other ruthenium(III) complexes[25,26].

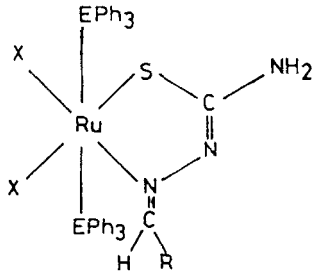
Electrochemistry

Cyclic voltammetric studies were carried out for some of the ruthenium thiosemicarbazone complexes in acetonitrile solution at a glassy carbon working electrode. The redox potentials of the complexes are characterised by well defined waves in the range 0.57 V to 0.66 V (oxidation) and -0.69 V to -0.91 V (reduction) versus a saturated calomel electrode (SCE). The cyclic voltammetric data are given in Table IV. As the ligands used in this study are not reversibly reduced or oxidised within the potential limits of +1.0 V to -1.0 V, the observed redox processes are metal centered only. All the complexes show a reversible oxidation (Ru^{IV}-Ru^{III}) wave with a peak to peak separation (ΔEp) values ranging from 60 mV to 100 mV indicative of a single step, one-electron transfer process[27,28]. Most of the complexes show an ireversible reduction wave (Ru^{III}-Ru^{II}) in the -0.69 V to -0.95 V range. A marked difference in the reduction behaviour is seen for $[RuCl_2(BTSC)(PPh_3)_2]$ and $[RuCl_2(CTSC)(AsPh_3)_2]$

Table IV. Cyclic Voltammetric Data for Some Ru(III) Thiosemicarbazone Complexes[a]

No.	Complex	Ru^{IV} - Ru^{III}				Ru^{III}-Ru^{II}			
		Epa(V)	Epc(V)	E_f(V)	Δ Ep(mV)	Epc(V)	Epa(V)	E_f(V)	Δ Ep(mV)
1.	$[RuCl_2(BTSC)(PPh_3)_2]$	0.61	0.54	0.58	70	-0.91	-0.83	-0.87	80
2.	$[RuCl_2(TCTSC)(PPh_3)_2]$	0.60	0.54	0.57	60	-0.95	-	-	-
3.	$[RuCl_2(FTSC)(PPh_3)_2]$	0.71	0.61	0.66	100	-0.82	-	-	-
4.	$[RuCl_2(CTSC)(AsPh_3)_2]$	0.70	0.62	0.66	80	-0.92	-0.83	-0.87	90
5.	$[RuBr_2(TCTSC)(PPh_3)_2]$	0.69	0.60	0.65	90	-0.70	-	-	-
6.	$[RuBr_2(BTSC)(AsPh_3)_2]$	0.62	0.56	0.59	60	-0.69	-	-	-

[a] Solvent: acetonitrile; supporting electrolyte [0.05 M] TBAP; concentration of the metal complex: 0.001 M; scan rate 100 mVS^{-1}; all potentials are referenced to saturated calomel electrode (SCE).



(X = Cl or Br; E = P or As; R = C_6H_5, $C_6H_5CH=CH$, 2-thiophene or 2-furan)

Fig. 2. Structure of Ru(III) Thiosemicarbazone Complexes

which showed a reversible reduction with Δ Ep in the range 80-90 mV. It has also been observed that there is not much variation in the redox potentials due to the substitution of triphenylphosphine by triphenylarsine in the complexes. From the electrochemical data, it is also inferred that the redox process of these thiosemicarbazone complexes occurs at a less positive potential than that of the β-diketonate complexes[26], which may be due to the fact that the nitrogen and sulphur donor atoms present in the thiosemicarbazone ligand are better σ-donors than the oxygen atom present in the β-diketone system.

Based on the above discussions, we propose the following tentative octahedral structure for all the new complexes (Fig. 2).

Antibacterial Activity

The *in vitro* antibacterial screening of the ligands (H-CTSC) and (H-TCTSC) and their ruthenium complexes viz.,

Table V. Antibacterial Activity of Ru(III) Thiosemicarbazone Complexes

No.	Compound	Diameter of Inhibition Zone (mm)	
		S. typhi(-)	*E. feacalis*(-)
1.	(H-CTSC)	7	9
2.	$[RuCl_2(CTSC)(PPh_3)_2]$	12	11
3.	(H-TCTSC)	15	13
4.	$[RuCl_2(TCTSC)(PPh_3)_2]$	17	16

Concentration of the solution 500 $\mu gm\ L^{-1}$

$[RuCl_2(CTSC)(PPh_3)_2]$ and $[RuCl_2(TCTSC)(PPh_3)_2]$ was carried out against **Solemonella typhi** (gram -ve) and **Eenterobacteria feacalis** (gram -ve) using nutrient agar (NA) medium by agar-well diffusion method[29] (incubation period 18-24 h at 37°C). The test solutions were prepared in DMF. Of the four compounds tested, the ligand (H-TCTSC) and the ruthenium complex $[RuCl_2(TCTSC)(PPh_3)_2]$ were found to be more toxic against both species of bacteria than the other ligands and complexes. The increased activity of these two compounds may possibly be due to the presence of a thiophene moiety in their structure[30]. It is also been observed from the antibacterial screening studies that the ruthenium chelates have a higher activity than the respective free ligands against the same microorganism under identical experimental conditions (Table V), which is consist with earlier report[31]. The possible mode of increased toxicity of complexes than the free ligands may be explained in terms of Tweedy's chelation theory[32]. Chelation reduces considerably the polarity of the metal ion, because of partial sharing of its positive charge with the ligand, which favour its permeation into the normal cell process of bacteria.

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