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Organic Compounds of Lanthanide Elements. Part IV. Alcoholates of Praseodymium and Neodymium Chlorides

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The reactions of anhydrous praseodymium and neodymium chlorides have been studied with different alcohols methanol, ethanol, isopropanol, and n-butanol) and compounds of the type MCl_3. 3ROH have been isolated. Their trichloride monohydrates yield compounds with the general formula $MCl_3.H_2O.2$ ROH. The higher alcoholates could also be synthesized from lower alcoholates by alcohol-interchange technique. The conductances of alcoholic solutions of anhydrous praseodymium chloride in methanol and ethanol have been measured. A spectrophotometric study of neodymium chloride tri-alcoholates (methanol, ethanol, and isopropanol derivatives) has been made.

The preparation and properties of alkoxides and alcoholate derivatives of transition elements have been extensively studied[1-3], but only a few references are available on similar derivatives of inner-transition elements. Meyer and Koss[4] reported that a crystalline solid, $LaCl_3.2C_2H_5OH$, separated from the ethanolic solution of lanthanum chloride El-Aggan *et al*[5]. have recently reported the synthesis of isopropanol derivative of lanthanum chloride, $LaCl_3$. 3 *i*-PrOH by alcoholysis of the corresponding ethanol compound, isolated during the azeotropic drying of hydrated lanthanum chloride. Alcoholate derivatives of lanthanum and cerium(III) chlorides have already been described[1]. In view of the above, it was considered worthwhile to make an extensive study of the corresponding derivatives of praseodymium and neodymium.

The anhydrous chlorides of praseodymium and neodymium were found to dissolve in methanol, ethanol, isopropanol, and n-butanol to provide alcoholates of the general formula $MCl_3.3$ ROH.

$$MCl_3 + 3\,ROH \longrightarrow MCl_3 . 3\,ROH$$

The solubility of the chlorides and the amount of heat evolved during dissolution of these chlorides decrease with the increasing molecular weight of the parent alcohol. The refluxing of the metal chlorides with the alcohol was found essential for their complete dissolution in cases of isopropanol and n-butanol. Removal of the excess alcohols (under reduced pressure and room temperature) from the clear alcoholic solutions, thus obtained, yielded products which corresponded in analysis closely to the tri-alcoholates. The tri-alcoholates of praseodymium and neodymium, thus isolated, are green and reddish violet solids, respectively, highly soluble in the parent alcohol, and insoluble in benzene alone;

1. Misra *et al.*, *J. Inorg. Nucl. Chem.* (In press).
2. Bradley, "Metal Alkoxides: Progress in Inorganic Chemistry" by Cotton' Vol. II, Interscience Publishers Inc., New York, 1960, p. 303.
3. Kapoor, Ph. D. thesis, London University, 1960.
4. Meyer and Koss, *Ber.*, 1902, 35, 2740.
5. *J. Chem. Soc.*, 1958, 2092.

but these dissolve in benzene also when a little alcohol is added. Out of these, only the isopropanol derivatives (MCl_3. 3 *i*-PrOH) could be recrystallised from their alcoholic solution in the form of characteristic needle-like crystals and thus these could be prepared in a state of high purity. Interestingly, in the case of other metals like thorium[6], uranium[3], and chromium[7] also, the isopropanol derivative is the only one which has a pronounced tendency of crystallising from the parent alcohol. When the chlorides were refluxed with *sec.*-butanol, products with an appreciably lower metal to chlorine ratio (approximately 1:2.2) were obtained, indicating the occurrence of some side reactions. The side decompositions were found to be even more marked in the reaction of praseodymium chloride with *t*-butanol, in which case a light green, insoluble solid with metal to chlorine ratio as low as about 1:0.7 was obtained.

During the course of the above investigations, observations were repeatedly made which appeared to confirm the work of Meyer and Koss[4] who reported the formation of di-alcoholate derivative only. The samples of chlorides, obtained by evaporating praseodymium and neodymium oxides in hydrochloric acid, appeared to hold a molecule of water. Such samples on treatment with methanol, ethanol, and isopropanol provided di-alcoholates of the type $MCl_3.H_2O$. 2ROH. The tri-alcoholates (MCl_3. 3 ROH), however, could be prepared by the reaction of alcohols with anhydrous chlorides obtained by heating the monohydrates in a current of dry HCl gas. These di-alcoholates appeared to hold the molecule of water more tenaciously than the alcohol molecules. On treatment with the required quantity of *n*-butanol, it could be converted quantitatively into its corresponding *n*-butanol derivative without affecting the water content:

$$MCl_3.H_2O.2\ i\text{-PrOH} + 2\ n\text{-BuOH}$$

$$\xrightarrow[\text{benzene}]{\text{Excess}} MCl_3.H_2O.\ 2\ n\text{-BuOH} + (2\ i\text{-PrOH} + C_6H_6)$$

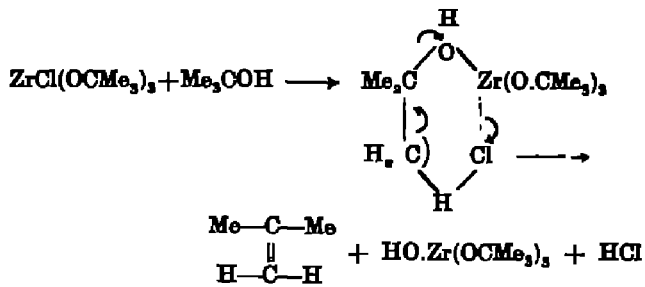
The di-isopropanolates could, however, be quantitatively converted into tri-isopropanolates by refluxing with a large excess of isopropanol in presence of benzene when the ternary water-alcohol-benzene azeotrope was continuously fractionated.

As described earlier[1], the direct reaction of anhydrous metal chloride with secondary and tertiary butanols led to side reactions with replacement of chlorine also. In view of the above observations, the azeotropic technique was attempted for the conversion of praseodymium and neodymium chloride tri-alcoholates to the corresponding butanol derivatives. Thus *n*-butanol was found to interchange with the three alcohol molecules when required quantities of the two reactants were refluxed with excess of benzene for several hours. The products, obtained after the slow removal of the azeotrope and drying under vacuum, corresponded in analysis to MCl_3. 3 *n*-BuOH. The metal : chlorine ratio in the product of neodymium chloride tri-isopropanolate and *sec.*-butanol reaction was about 1 : 2.80 and that in praseodymium chloride tri-isopropanolate–*t*-butanol reaction was about 1:0.7.

Similar tendencies of decomposition had been observed when chlorides or chloride alkoxides of other metals were treated with an excess of tertiary alcohol. The mechanism

6. Bradley *et al.*, *J. Chem. Soc.*, 1954, 2002.
7. Mehrotra and Sharma, private communication.

for this type of reactions was initially proposed by Bradley *et al*[8]. According to them, the reaction of excess of *t*-butanol and zirconium chloride alkoxide provided a decomposed product along with alkyl chloride and olefine. In view of the decisive role played by the excess of tertiary alcohols : the following mechanism,



was proposed. Provided that the central atom of the metal halide alkoxide has a tendency to co-ordinate in this position, the subsequent electronic rearrangement occurs chiefly as a consequence of the properties of tertiary alcohols and a similar mechanism would be expected to be operative in the case of praseodymium and neodymium chlorides.

The same authors[8] have also pointed out that the decompositions, described above, might possibly be occurring by a different mechanism, involving the formation of carbonium ions:

$$MCl_3 . 3\,ROH \longrightarrow [MCl_3 . (OH) . 2\,ROH]^- + R^+$$

$$[MCl_3 . (OH) . 2\,ROH]^- \longrightarrow MCl_3(OH) . 2\,ROH + Cl^-$$

followed by

$$R^+ + Cl^- \longrightarrow RCl$$

$$R^+ + ROH \longrightarrow \text{olefine} + [ROH_2]^+$$

$$[ROH_2]^+ + Cl^- \longrightarrow ROH + HCl$$

It is evident that further detailed mechanistic studies will be required to elucidate the observed behaviour of tertiary alcohols towards metal halides.

In investigating the pyrolytic behaviour of praseodymium and neodymium chloride tri-isopropanolates, these compounds were heated under reduced pressure (0.05 mm) for seventy minutes at different temperatures. These were found to be stable to 50° under the above experimental conditions, beyond which decomposition started when the isopropanol molecules of addition appeared to be lost with very slight decomposition of the trichlorides even at higher temperatures.

The conductance of praseodymium chloride was measured in dry methanol and ethanol in the concentration range of 10^{-4} to 10^{-3} moles. At these dilutions the chloride was observed to be only partially dissociated. The plots of Δm (molecular conductance) against $\sqrt{c}$ (concentration) provided a straight line and the extrapolated values for the limiting molecular conductance in methanol and ethanol were found to be 72.5 and 28.0, respectively. These low values indicate that praseodymium chloride is only partially dissociated in alcoholic solutions.

$$PrCl_3 \rightleftharpoons Pr\,Cl_2^+ + Cl^-$$

8. *J. Chem. Soc.*, 1952, 4960.

The absorption spectra measurements of different neodymium chloride alcoholate solutions in the parent alcohols were carried out in the visible region. The results obtained are plotted in Fig. 1-3 In almost all the cases studied, some prominent bands are observed at wave lengths 515, 525, 582, 745, 805, and 875 mμ with only a slight variation with the change of solvent. In addition to these sharp bands, some less-defined bands are also detectable at wave lengths 430, 475, and 680 mμ. Incidentally, $NdCl_3$ in aqueous solutions shows[9] principal absorption bands at 354, 522, 575, 740, 742, 798, 803, and 868 mμ.

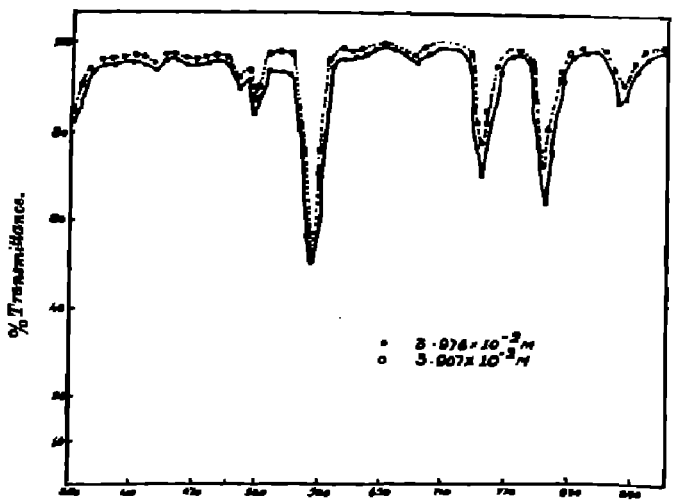


Fig. 1. Neodymium trichloride trimethyl alcoholate.

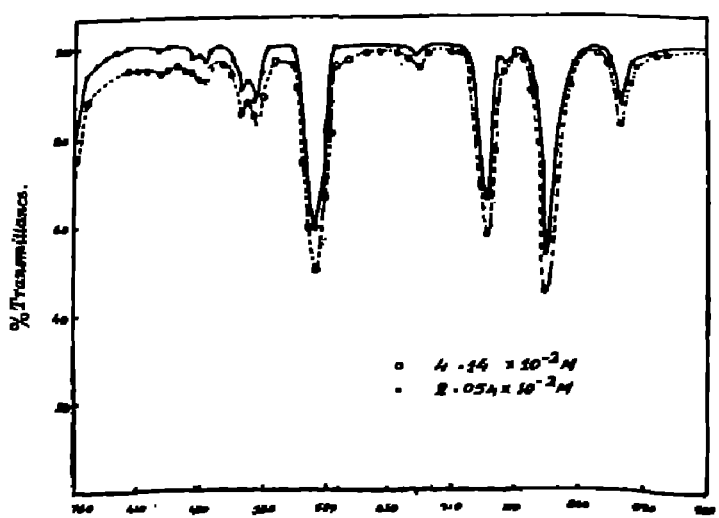


FIG. 2. Neodymium trichloride triethyl alcoholate.

9. Moeller and Brantley, *Anal. Chem.*, 1950, 22, 433.

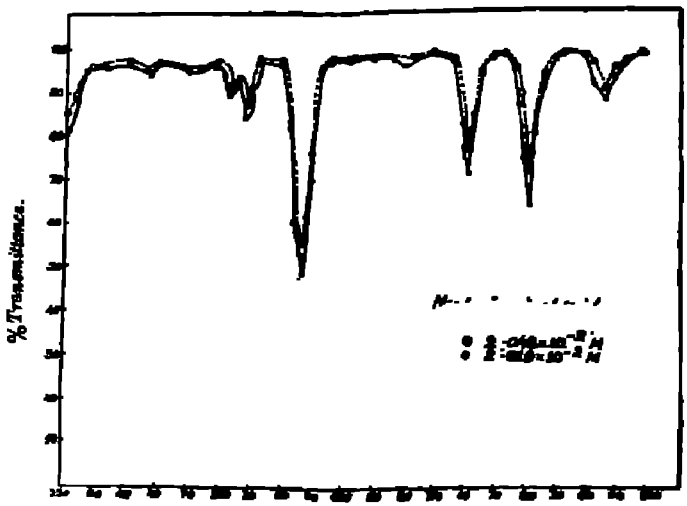


FIG. 3. Neodymium trichloride tri-isopropyl alcoholate.

EXPERIMENTAL

Methanol, ethanol, and propanols were dried by refluxing them with metallic sodium, followed by fractional distillation with a small amount of benzene. Butanols were dried by refluxing them over their respective sodium alkoxides. Benzene was kept over sodium wire, refluxed with metallic sodium, and finally dried azeotropically with a little ethanol.

Anhydrous praseodymium and neodymium chlorides were prepared from their oxides (Johnson Matthey, 99.9%). The solutions of these oxides in HCl (conc.) were evaporated to dryness and the mass was powdered and dissolved again in the acid; the operation was repeated four times. The samples, thus obtained, were found to hold a molecule of water of hydration. Finally, anhydrous samples were obtained by heating the above product in a stream of dry HCl gas.

Praseodymium and neodymium were estimated as their oxides by first precipitating them as oxalates. Alcohols (methanol, ethanol, and isopropanol) in the compounds or in the azeotrope were determined by the chromic acid oxidation method[10].

All-glass apparatus with standard interchangeable joints was used throughout this investigation. A Phillips magic eye type (P. R. 9500) conductivity bridge was used for conductance measurements. The measurements of optical absorbance were carried out with a Beckman spectrophotometer (model D.U. 2400) employing a silica cuvette.

Preparation of Tri-alcoholates of Praseodymium and Neodymium Chlorides: Reaction between Anhydrous Praseodymium Chloride and Isopropanol

Isopropanol (26.0 g.) was added to anhydrous praseodymium chloride (2.4 g.) when a mild exothermic reaction was found to occur with partial dissolution of the chloride.

10. Mehrotra, this *Journal*, 1953, **36**, 585; 1954, **31**, 904.

TABLE I

	Metal chloride.	Alcohol.	Formula.	% Metal. Found.	% Metal. Reqd.	% Chlorine. Found.	% Chlorine. Reqd.	% Alcohol. Found.	% Alcohol. Reqd.	Molar ratio. M/Cl.	Molar ratio. M/alc.
1	$PrCl_3$	MeOH	$PrCl_3.3CH_3OH$	40.60	41.03	30.60	30.98	27.80	27.99	1/3.00	1/3.00
2	$NdCl_3$		$NdCl_3.3CH_3OH$	41.30	41.60	30.60	30.68	27.40	27.72	1/3.00	1/2.99
3	$PrCl_3$	EtOH	$PrCl_3.3C_2H_5OH$	36.30	36.56	27.40	27.59	35.30	35.85	1/3.00	1/3.00
4	$NdCl_3$	,,	$NdCl_3.3C_2H_5OH$	36.50	37.10	27.40	27.36	35.10	35.54	1/3.00	1/3.00
5	$PrCl_3$	i-PrOH	$PrCl_3.3i\text{-}C_3H_7OH$	32.80	32.96	24.80	24.87	42.10	42.17	1/3.00	1/3.00
6	$NdCl_3$	,,	$NdCl_3.3i\text{-}C_3H_7OH$	33.70	33.48	24.60	24.69	41.750	41.83	1/2.97	1/2.97
7	$PrCl_3$	n-BuOH	$PrCl_3.3n\text{-}C_4H_9OH$	30.20	30.00	22.80	22.65	..	..	1/3.00	..
8	$NdCl_3$	,,	$NdCl_3.3n\text{-}C_4H_9OH$	30.80	30.50	22.80	22.49	..	..	1/2.93	..
9	$PrCl_3$	i-BuOH	$PrCl_3.3i\text{-}C_4H_9OH$	30.20	30.00	22.80	22.65	..	..	1/3.00	..
10	$NdCl_3$	,,	$NdCl_3.3i\text{-}C_4H_9OH$	31.10	30.50	22.70	22.49	..	..	1/2.91	..
11	$PrCl_3$	sec.-BuOH	..	38.10	30.00	20.40	22.65	..	..	1/2.13	..
12	$NdCl_3$	,,	..	54.30	30.50	29.550	22.49	..	..	1/2.21	..
13	$PrCl_3$	t-BuOH	..	58.40	30.00	10.80	22.65	..	..	1/0.73	..

TABLE II

	Metal chlorides.	Alcohol.	Formula.	% Metal. Found.	% Metal. Reqd.	% Chlorine. Found.	% Chlorine. Reqd.	% Alcohol. Found.	% Alcohol. Reqd.	Molar ratio M/Cl.	Molar ratio M/alc.
1	$PrCl_3$	MeOH	$PrCl_3.H_2O.2CH_3OH$	42.80	42.70	32.30	32.30	20.20	20.20	1/3.0	1/2.0
2	$NdCl_3$	,,	$NdCl_3.H_2O.2CH_3OH$	43.40	43.36	32.20	31.97	19.30	19.26	1/3.0	1/2.0
3	$PrCl_3$	EtOH	$PrCl_3.H_2O.2C_2H_5OH$	39.90	39.42	29.60	29.76	25.40	25.77	1/3.0	1/1.98
4	$NdCl_3$	,,	$NdCl_3.H_2O.2C_2H_5OH$	39.80	39.99	29.30	29.48	25.40	25.54	1/3.0	1/2.0
5	$PrCl_3$	i-PrOH	$PrCl_3.H_2O.2i\text{-}C_3H_7OH$	37.53	37.28	27.30	27.40	31.20	31.40	1/3.0	1/2.0
6	$NdCl_3$	,,	$NdCl_3.H_2O.2i\text{-}C_3H_7OH$	37.30	37.10	27.60	27.36	30.00	30.90	1/3.0	1/1.98

The reactants were refluxed for 2 hr. when a clear green solution was obtained. On cooling to the room temperature, green needle-like crystals separated from the mother liquor. After removal of the upper liquor by decantation, drying of the product at 27°/10.1 mm yielded a green crystalline solid. The product was recrystallised from isopropanol, yield 3.2 g. (Found: Pr, 32.80; Cl, 24.90; *i*-PrOH, 42.10. $PrCl_3.3$ *i*-PrOH requires Pr, 32.96; Cl, 24.87; *i*-PrOH, 42.17%). Thus several similar derivatives have been synthesised and the results obtained during such investigations are summarised in Table I.

Di-alcoholates of Praseodymium and Neodymium Chlorides: Preparation of Praseodymium Chloride Monohydrate Di-isopropanolate

Praseodymium chloride monohydrate (4.4 g.) was refluxed with isopropanol (65.0 g.) for 2 hr. The green solution, thus obtained, containing some undissolved impurities, was separated while hot through a transfer tube. After cooling, a green compound crystallised from the mother liquor. On drying at 26°/0.2 mm, a benzene-insoluble crystalline solid (6.3 g.) was obtained. (Found: Pr, 37.50; Cl, 27.30; *i*-PrOH, 31.20. $PrCl_3.H_2O.2$ *i*-PrOH requires Pr, 37.28; Cl, 27.40; *i*-PrOH, 31.40%). Pr/Cl is 1/2.94; Pr/*i*-PrOH is 1/1.92. Several di-alcoholates of praseodymium and neodymium prepared are recorded in Table II.

Preparation of Higher Alcoholates from Lower Ones by Alcohol-interchange Reactions: Reaction of Praseodymium Chloride Tri-ethanolate with n-Butanol in Benzene

n-Butanol (5.0 g.) was added to praseodymium chloride tri-ethanolate (2.2 g.) in benzene (45.0 g.). The contents were refluxed for about 3 hr. The ethanol-benzene azeotrope (68°) was first collected and finally excess of the solvent was removed by distillation. A green solid (3.3 g.) was obtained after drying the product at 27°/0.1 mm. (Found: Pr, 30.20; Cl, 22.60. $PrCl_3.3$ *n*-BuOH requires Pr, 30.00; Cl, 22.65%).

Several alcohol-interchange reactions were carried out by taking both di- and tri-alcoholates of praseodymium and neodymium chlorides as starting meterials. The results are recorded in Table III.

TABLE III

	Starting material.	Alcohol added.	Formula.	% Metal. Found.	% Metal. Reqd.	% Chlorine. Found.	% Chlorine. Reqd.	Molar ratio (M/Cl).
1	$PrCl_3$ monohydrate di-isopropanolate	*n*-BuOH	$PrCl_3.H_2O.2n$-BuOH	34.50	34.24	25.40	25.60	1/2.93
2	$PrCl_3$ tri-ethanolate	,,	$PrCl_3.n$-3BuOH	30.20	30.00	22.60	22.65	1/2.99
3	$NdCl_3$ tri-isopropanolate	,,	$NdCl_3.n$-3BuOH	30.80	30.50	22.00	22.49	1/3.00
4	$NdCl_3$ tri-ethanolate	,,	$NdCl_3.3n$-BuOH	30.40	30.50	22.45	22.49	1/3.00
5	$NdCl_3$ tri-isopropanolate	sec.-BuOH	..	52.30	30.50	35.80	22.49	1/2.78
6	$PrCl_3$ tri-isopropanolate	*t*-BuOH	..	60.10	30.09	10.09	22.65	1/0.26

Conversion of Di-alcoholates to Tri-alcoholates

(*i*). *Reaction of Praseodymium Chloride Monohydrate Di-isopropanolate with Excess Isopropanol in Benzene.*—Praseodymium chloride monohydrate di-isopropanolate (3.2 g.) was dissolved in a mixture of benzene (67.0 g.) and isopropanol (11.9 g.). The reaction mixture was refluxed for several hours. The ternary azeotrope (water-alcohol-benzene) was slowly collected; excess of the solvent was then distilled and finally a green solid (3.6 g) was obtained after freeing the contents from the solvents under reduced pressure. (Found: Pr, 33.00; Cl, 24.70; *i*-PrOH, 42.00. $PrCl_3$. 3 *i*-PrOH requires Pr, 32.96; Cl, 24.87; *i*-PrOH, 42.17%).

(*ii*). *Reaciton between Neodymium Chloride Monohydrate Di-isopropanolate and Excess Isopropanol in Benzene.*—Isopropanol (14.0 g.) was added to neodymium chloride monohydrate di-isopropanolate (2.25 g.) in benzene (75.0 g.). The mixture was refluxed under a long fractionating column (130 cm) for about 8 hr. The ternary azeotrope (66.5°) was first collected carefully, followed by fractionation of the binary azeotrope (isopropanol-benzene) along with the removal of excess of the solvent. A reddish violet crystalline solid (2.41 g.) was obtained after drying the product at 25°/0.3 mm. (Found: Nd, 34.60; Cl, 24.40; *i*-PrOH, 40.80. $NdCl_3$. 3*i*-PrOH requires Nd, 33.48; Cl, 24.69; *i*-PrOH, 41.83%).

Effect of Heat on Alcoholates

Praseodymium and neodymium chloride tri-isopropanolates were heated under reduced pressure at different temperatures for a definite period. The results obtained during the course of such studies are described in Table IV (A and B).

TABLE IV

Effect of heat at 0. 05 mm for 70 min.

Temp.	%Metal.	%Chlorine.	%Alcohol.	M/Cl.	M/alc.
		A. $PrCl_3$.3 *i*-PrOH.			
50°	32.7	25.1	40.5	1/3.0	1/2.94
60°	35.2	26.9	36.0	1/2.94	1/2.34
70°	38.3	29.9	32.9	1/2.9	1/2.0
100°	52.5	37.0	9.9	1/2.8	1/0.42
125°	55.7	38.4	4.6	1/2.8	1/0.2
		B. $NdCl_3$.3 *i*-PrOH			
600	46.3	32.25	20.5	1/2.83	1/1.06
750	51.2	35.70	12.3	1/2.82	1/0.58
1000	55.7	38.05	4.5	1/2.78	1/0.2

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