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Solvent Extraction of Rare Earth Metal Ions with 1-(2-Pyridylazo)-2-Naphthol (*PAN*)

V. Complex Formation and Distribution Equilibria of Thulium(III) with *PAN*

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The formation of the Tm(III) complex with 1-(2-pyridylazo)-2-naphthol (*PAN* or H*L*) in aqueous-methanol mixtures (50 and 75% *v/v*) was studied by a spectrophotometric method. The equilibrium constant for the complexing reaction and the stability constant of the complex $\mathrm{Tm}L^{2+}$ were calculated. The solvent extraction of Tm(III) by *PAN* in carbon tetrachloride from aqueous and aqueous-methanol phase was investigated. The extraction equilibrium constants and two-phase stability constants for the $\mathrm{Tm}L_3$ and the $\mathrm{Tm}L_3(Me\mathrm{OH})_3$ complexes were evaluated. It was confirmed that the addition of methanol to the aqueous phase (above 25% *v/v*) causes a synergistic effect.

[Keywords: Complexes; Extraction; 1-(2-Pyridylazo)-2-naphthol; Stability constants; Thulium(III)]

Extraktion von Ionen der Seltenerdmetalle mit 1-(2-Pyridylazo)-2-naphthol (PAN), 5. Mitt.: Komplexbildung und Gleichgewichtsverteilung von Thulium(III) mit PAN

Die Bildung des Komplexes von Tm(III) mit 1-(2-Pyridylazo)-2-naphthol (*PAN* oder H*L*) in Wasser-Methanol Mischungen (50 und 75% *v/v*) wurde mit einer spektrophotometrischen Methode untersucht. Die Gleichgewichtskonstante für die Reaktion der Komplexbildung und die Stabilitätskonstante des Komplexes $\mathrm{Tm}L^{2+}$ wurden berechnet. Die Extraktion von Tm(III) mittels *PAN* in Kohlenstofftetrachlorid aus Wasser oder Wasser-Methanol wurde untersucht. Die Werte der Extraktionsgleichgewichtskonstante sowie der zweiphasigen Beständigkeitskonstante für die Komplexe $\mathrm{Tm}L_3$ und $\mathrm{Tm}L_3(Me\mathrm{OH})_3$ wurden berechnet. Es wurde festgestellt, daß die Zugabe von Methanol zur wäßrigen Phase (~ 25% *v/v*) einen synergistischen Effekt hat.

Introduction

In our previous studies [1–7] we have shown the influence of aliphatic alcohols on the complex formation and the extraction of lanthanides(III) with 1-(2-pyridylazo)-2-naphthol (*PAN* or H*L*). It was observed that the presence of methanol or ethanol in aqueous phase causes a synergistic effect in the extraction of Yb(III), Ho(III), Lu(III), and Dy(III) with *PAN* in CCl_4 [1–4]. Moreover, it was found that the stability constants of lanthanide(III) complexes with *PAN* depend largely on the kind and the concentration of aliphatic alcohols [4–7].

The present paper is undertaken to investigate the extraction of Tm(III) with *PAN* in carbon tetrachloride from aqueous and aqueous-methanol (polar) phase. The process of complexing with *PAN* in water-methanol mixtures was studied by a spectrophotometric method.

Experimental

A solution of thulium perchlorate was obtained by dissolving Tm_2O_3 (Johnson Matthey Chemicals Ltd, specpure) in 3 mol/dm^3 perchloric acid, diluted with water and standardized [8].

Stock solutions of 1-(2-pyridylazo)-2-naphthol (POCh-Gliwice p. a.) in methanol ($d = 0.791$ g/cm^3, POCh-Gliwice p. a.) or carbon tetrachloride (POCh-Gliwice p. a.) were prepared by weighing and then diluted to the predetermined concentrations with the appropriate solvent.

The experimental procedure, the calculations, the instruments and other reagents were the same as reported earlier [1, 5, 9].

The formation of *PAN* complexes in the system: Tm(III)—*PAN*—*Me*OH—H_2O was investigated by a spectrophotometric method as previously [5]. At variable concentrations of metal ions or *PAN* absorption spectra of the complexes in 50 and 75% *v*/*v* *Me*OH were recorded. As an example Figs. 1 and 2 show the absorption spectra for the system: Tm(III)—*PAN*—50% *v*/*v* *Me*OH.

In extraction experiments the concentrations of Tm(III) in aqueous or aqueous-methanol phase was always 50 μg/cm^3, the initial concentration of methanol in the polar phase (C_{MeOH}) and *PAN* in the organic phase (C_{HL}) varied from 5 to 50% *v*/*v* and from $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ mol/dm^3, respectively.

The distribution coefficient (*D*) was calculated from the equilibrium concentration of Tm(III) in the organic phase (after reextraction) and aqueous (or polar) phase. The extent of extraction (%*E*) was calculated as previously [9].

Figure 3 represents the dependence of %*E* vs. *pH* of aqueous or pH^x of the aqueous-methanol phase ($pH^x = -\lg[H^+]$ in aqueous-methanol solution [10]). It was observed that in the presence of methanol in the polar phase (Fig. 3, curve 2) the extraction of Tm(III) occurs at a lower *pH* range than in its absence ($pH_{0.5} = 6.55$ and $pH^x_{0.5} = 5.95$).

Studies on the extraction equilibria were carried out in series using different parameters: *pH* (or pH^x), concentrations of *PAN* or *Me*OH [1, 9].

Results and Discussion

Absorption measurements of the Tm(III)—*PAN*—methanol—water system indicated the formation of complexes (Figs. 1 and 2). Similarly, as

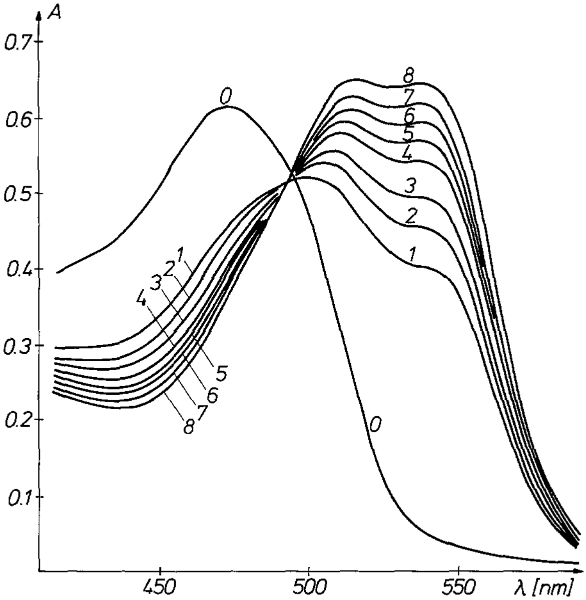

Fig. 1. Absorption spectra of *PAN* in the presence of Tm(III) in 50% *v*/*v* methanol. Concentration of *PAN*—$3.5 \cdot 10^{-5}$ mol/dm^3, Tm(III) concentration $C_{\mathrm{Tm}} \cdot 10^4$ mol/dm^3 for curves: *0* 0.00; *1* 1.40; *2* 2.10; *3* 2.80; *4* 4.20; *5* 5.60; *6* 7.00; *7* 9.80; *8* 14.00; $pH^* = 5.95$

for others lanthanides [5–7] the isosbestic point in the absorption spectra of *PAN* at different concentration of Tm(III) (Fig. 1) was observed. On the basis of spectrophotometric data and at the same conditions existing in the extraction process in aqueous-methanol phase, the presence of the $\mathrm{Tm}L^{2+}$ complex was established by the straight line method [11]. The equilibrium constants (*K*) of the reaction:

$$\mathrm{Tm}^{3+} + \mathrm{H}L \overset{K}{\rightleftharpoons} \mathrm{Tm}L^{2+} + \mathrm{H}^+ \qquad (1)$$

were obtained using the *Watters* method [5, 12]. The calculations of *K* were performed by the method of least squares. Figure 4 shows the graphic determination of equilibrium constants (*K*). Stability constants (β_1) of complex $\mathrm{Tm}L^{2+}$ in 50 and 75% *v*/*v* *Me*OH were evaluated using the expression $\beta_1 = K/K_{\mathrm{OH}}$ (where K_{OH} is the dissociation constant of *PAN* in methanol-water solution [6, 13]). The values of the constants *K* and β_1 were: $pK = 2.27$, $\lg \beta_1 = 9.73$ in 50% *v*/*v* *Me*OH and $pK = 1.61$, $\lg \beta_1 = 11.29$ in 75% *v*/*v* *Me*OH (correlation coefficient $\Delta_{pK} = 0.97$ and 0.96).

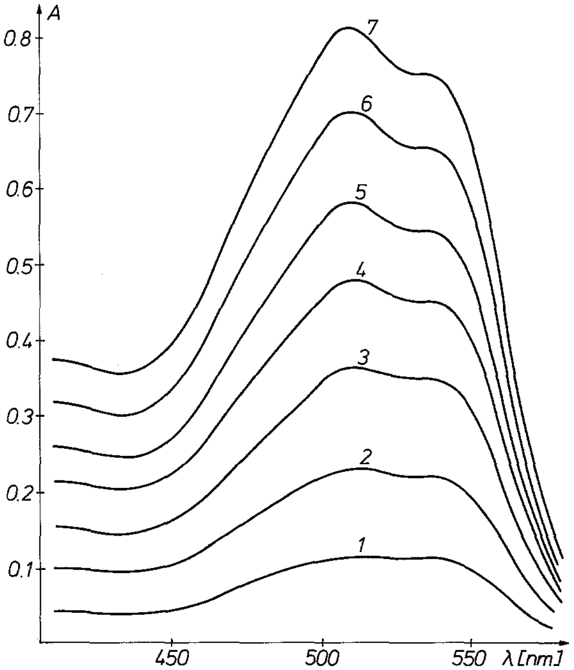

Fig. 2. Absorption spectra of Tm(III) in the presence of *PAN* in 50% v/v methanol. Concentration of Tm(III)—$4.20 \cdot 10^{-4}$ mol/dm^3, *PAN* concentration $C_{HL} \cdot 10^5$ mol/dm^3 for curves: *1* 0.70; *2* 1.40; *3* 2.10; *4* 2.80; *5* 3.50; *6* 4.20; *7* 4.90; $pH^x = 6.05$

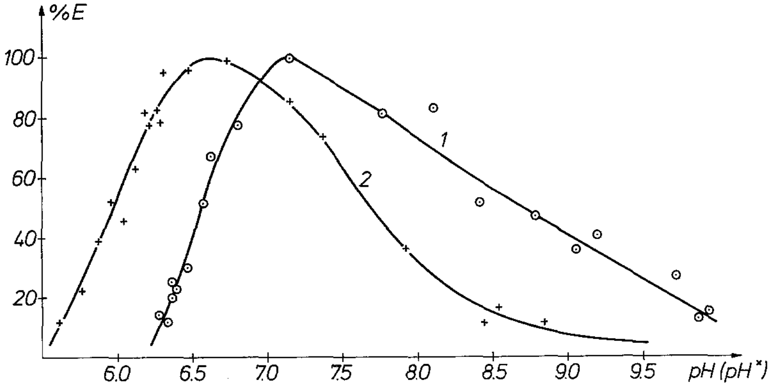

Fig. 3. The efficiency of Tm(III) extraction with *PAN* in CCl_4 from the phases: *1* aqueous; *2* 50% v/v methanol; $C_{Tm} = 50\,\mu g/cm^3$; $[HL]_{(0)} = 1.00 \cdot 10^{-2}$ mol/dm^3

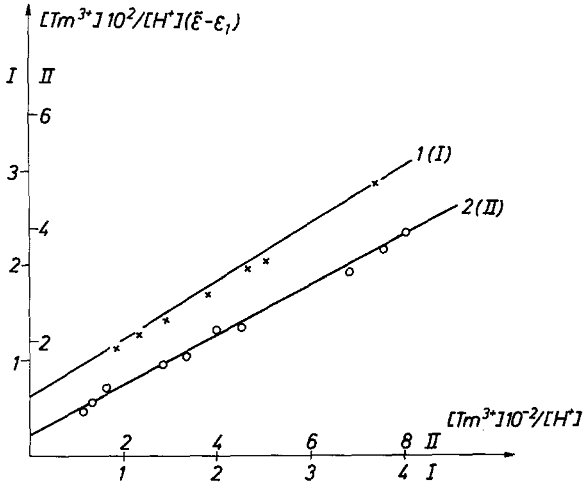

Fig. 4. *Watter*'s method plot of $[\mathrm{Tm}^{3+}]\,10^2/[\mathrm{H}^+](\bar{\varepsilon}-\varepsilon_1)$ vs. $[\mathrm{Tm}^{3+}]\,10^{-2}/[\mathrm{H}^+]$ for the system: Tm(III)—*PAN*—methanol—water. Curves: *1* in 50% *v/v* methanol, *2* in 75% *v/v* methanol ($\bar{\varepsilon}$: mean absorption coefficient; ε_1 : absorption coefficient of *PAN*)

An increase in the stability constants of the complex $\mathrm{Tm}L^{2+}$ by increasing the concentration of methanol was found. The values of stability constants of the complex $\mathrm{Tm}L^{2+}$, according to the dependence of $\lg\beta_1$ vs. the atomic number of lanthanides [5], appear between the values of β_1 for $\mathrm{Er}L^{2+}$ and $\mathrm{Yb}L^{2+}$.

The distribution equilibria of Tm(III) with *PAN* from aqueous or aqueous-methanol phase were investigated in the *pH* range 6.2–6.9 and pH^x range 5.5–6.5. At higher *pH* (or pH^x) a turbidity of aqueous (or polar) phase and the occurrence of a suspension at the phase boundary was observed.

Similarly as in the previous papers [1, 3] the equations of the extraction of Tm(III) with *PAN* from aqueous-methanol medium can be generally written as:

$$\mathrm{Tm}^{3+} + (3+n)\mathrm{H}L_{(0)} + t\,Me\mathrm{OH}_{(0)} \overset{K_{\mathrm{ex}}}{\rightleftharpoons}$$

$$\overset{K_{\mathrm{ex}}}{\rightleftharpoons} \mathrm{Tm}L_3(\mathrm{H}L)_n(Me\mathrm{OH})_{t(0)} + 3\,\mathrm{H}^+ \tag{2}$$

and

$$\lg D + \lg\left(1 + \sum_{i=0}\sum_{j=0}\sum_{q=0}\beta_{ijq}[\mathrm{OH}^-]^i[L^-]^j[X]^q\right) =$$

$$= \lg K_{\mathrm{ex}} + 3\,pH^x + (3+n)\lg[\mathrm{H}L]_{(0)} + t\lg[Me\mathrm{OH}]_{(0)} \tag{3}$$

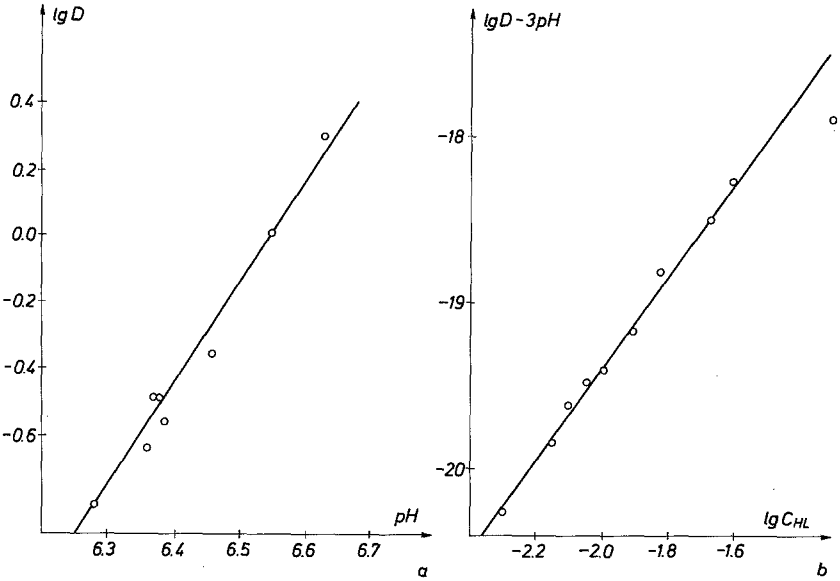

Fig. 5. The graphic solving of Eq. (3) for the extraction of Tm(III) with *PAN* from aqueous phase, $C_{\mathrm{Tm}} = 50\,\mu\mathrm{g/cm^3}$; *a* $C_{\mathrm{H}L} = 1.00 \cdot 10^{-2}\,\mathrm{mol/dm^3}$; *b* $C_{\mathrm{H}L}$ from $2.50 \cdot 10^{-2}$ to $5.00 \cdot 10^{-3}\,\mathrm{mol/dm^3}$

where the subscript (0) denotes the organic phase, K_{ex} is the extraction constant, β_i, β_j, β_q are the stability constants of $\mathrm{Tm(OH)}_i^{3-i}$, $\mathrm{Tm}L_j^{3-j}$ and $\mathrm{Tm}X_q^{3-q}$ complexes, $X = \mathrm{ClO_4^-}$, hexamethylenetetramine.

It is obvious that for the extraction of Tm(III) from aqueous phase Eqs. (2) and (3) are simplified [9, 14]. However, in the extraction from aqueous-methanol phase the formation of Tm(III) complexes with *PAN* in this phase cannot be neglected.

The stoichiometry of the formation of extractable complex and the derivation of a suitable equilibrium expression by graphic solving of Eq. (3) was achieved.

In the extraction of Tm(III) from aqueous phase the number of protons released on chelation from the dependence lg *D* vs. *pH* (Fig. 5 a, slope 3) was determined. The plot ($\lg D - 3pH$) vs. lg $C_{\mathrm{H}L}$ (under investigated conditions $C_{\mathrm{H}L} = [\mathrm{H}L]_{(0)}$ [9]) yields a straight line of slope 2.8 (Fig. 5 b). Thus, in this range of *PAN* concentration three molecules of ligand participate in the extraction process.

Based on the obtained results the extraction of Tm(III) with *PAN* from aqueous phase may be described by the equation:

$$\mathrm{Tm}^{3+} + 3\,\mathrm{H}L_{(0)} \overset{K_{\mathrm{ex_{aq}}}}{\rightleftharpoons} \mathrm{Tm}L_{3(0)} + 3\,\mathrm{H}^+ \tag{4}$$

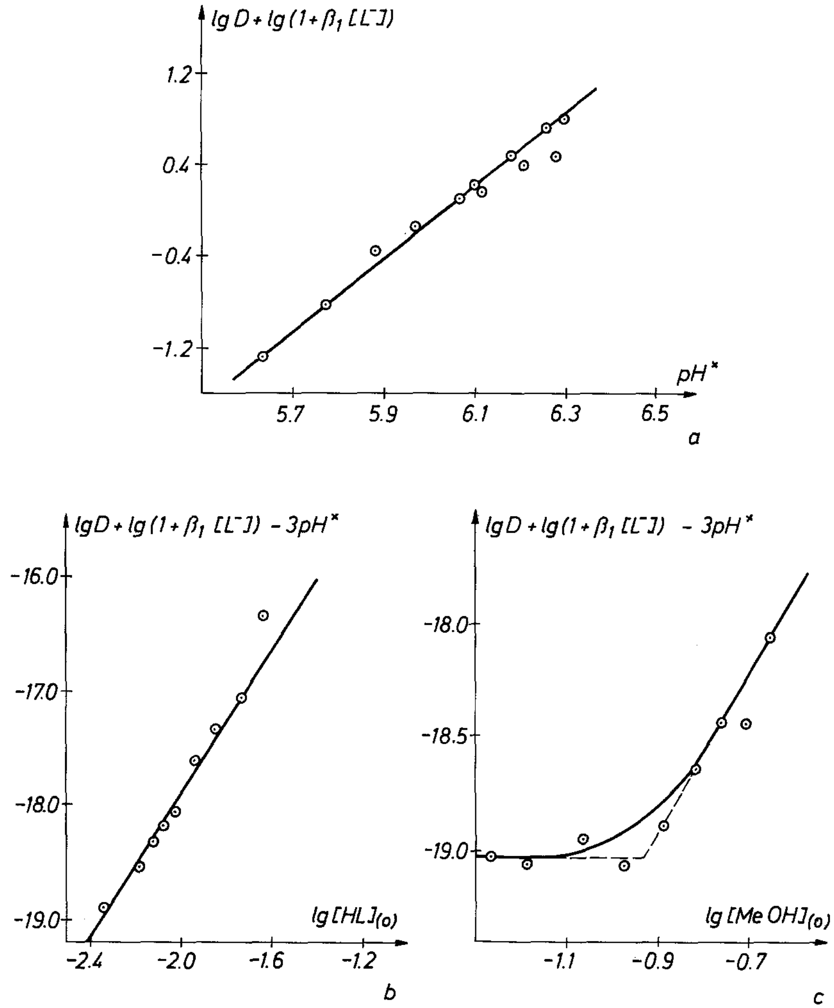

Fig. 6. The graphic solving of Eq. (3) for the extraction of Tm(III) with *PAN* from aqueous-methanol phase, $C_{\mathrm{Tm}} = 50\,\mu\mathrm{g/cm^3}$; *a* $[\mathrm{H}L]_{(0)} = 1.00 \cdot 10^{-2}\,\mathrm{mol/dm^3}$, $C_{Me\mathrm{OH}} = 50\%$ *v*/*v*; *b* $C_{Me\mathrm{OH}} = 50\%$ *v*/*v*, $C_{\mathrm{H}L}$ from $5.00 \cdot 10^{-2}$ to $5.00 \cdot 10^{-3}\,\mathrm{mol/dm^3}$; *c* $[\mathrm{H}L]_{(0)} = 1.00 \cdot 10^{-2}\,\mathrm{mol/dm^3}$, $C_{Me\mathrm{OH}}$ from 5 to 50% *v*/*v*

In the case of Tm(III) extraction from aqueous-methanol medium the graphic solving of Eq. (3) is given in Fig. 6. The number of protons from the dependence on Fig. 6 a (slope 3.0) was obtained. The number of *PAN* molecules is reflected in the slope (3.0) of dependence presented in Fig. 6 b. The number of *Me*OH molecules [*t* in Eq. (3)] from the slope of lg *D*

$+\lg(1+\beta_1[L^-]) = \mathrm{f}(\lg[Me\mathrm{OH}]_{(0)})$ was obtained (Fig. 6c). It is seen from Fig. 6c that for the initial concentration of MeOH in the polar phase (not exceeding the value of 25% v/v) the extraction of Tm(III) is independent on the MeOH concentration ($t = 0$). In the higher region of MeOH concentration (from 25 to 50% v/v) the extraction is dependent on the third order of $[Me\mathrm{OH}]_{(0)}$ ($t = 3$).

Table 1. *Values of* $\lg K_{ex}$, $\lg \beta^x$ *and* $pH_{0.5}^{(x)}$ *for the distribution of* Tm(III) *with PAN in* CCl_4 *[at 21 ± 1 °C,* $\mu = 0.1$ $(NaClO_4)$*]*

Extraction of Tm(III) from:	$\lg K_{ex}$ (∓ 0.03)	$\lg \beta^x$	$pH_{0.5}^{(x)}$
Aqueous phase	−13.55	32.02	6.55
Aqueous-methanol phase (for $C_{Me\mathrm{OH}} > 25\%$ v/v)	−10.11	27.93	5.95

The obtained data show that the extraction of Tm(III) from aqueous-methanol solutions may be described by the following reaction:

$$\mathrm{Tm}^{3+} + 3\,\mathrm{H}L_{(0)} + t\,Me\mathrm{OH}_{(0)} \overset{K_{\mathrm{ex}_{\mathrm{aq}\text{-}Me\mathrm{OH}}}}{\rightleftharpoons} \mathrm{Tm}L_3(Me\mathrm{OH})_{t(0)} + 3\,\mathrm{H}^+ \qquad (5)$$

where $t = 0$ for $C_{Me\mathrm{OH}} \in (\sim 5\text{–}25\%\ v/v)$, $t = 3$ for $C_{Me\mathrm{OH}} \in (\sim 25\text{–}50\%\ v/v)$.

For Eqs. (4) and (5) (in which $t = 3$) the values of $\lg K_{ex}$ were calculated by a least square procedure. Two-phase stability constants ($\lg \beta^x$) of the complexes $\mathrm{Tm}L_3$ and $\mathrm{Tm}L_3(Me\mathrm{OH})_3$ were calculated as earlier [1, 9]. The results are summarized in Table 1.

It is seen that the addition above 25% v/v MeOH to the aqueous phase increases K_{ex} about 1000 times. This fact is probably caused by the formation of the solvate $\mathrm{Tm}L_3(Me\mathrm{OH})_3$.

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