

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF RAJASTHAN, JAIPUR, INDIA

Some Reactions of Bismuth Trichloride in Dimethylformamide

BY A. K. MISHRA* AND K. N. TANDON

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Bismuth trichloride forms a 1:1 adduct with DMF (dimethylformamide). Its reactions in DMF have been studied conductometrically. With silver nitrate, a metathetical reaction occurs whereas with potassium iodide and di- or triethylammonium chloride, complex formation takes place. With bases like triethylamine and diethylamine, a quantitative solvolytic reaction occurs whereas with α -picoline and pyridine adduct formation together with a partial solvolytic reaction takes place. The solvolyzed products have been isolated and analyzed. These reactions throw light on the mode of ionization of bismuth trichloride in DMF.

Introduction

Dimethylformamide (DMF) has attracted some attention as a solvent only recently¹⁻¹¹ even though it possesses a convenient liquid range (-61 to $+150^\circ$), a fairly high dielectric constant (36.7), and specific conductivity $(0.6-2) \times 10^{-7}$ ohm⁻¹ at 25° (cf. specific conductivity of water). It has also been used as a solvent in nonaqueous titrations.²⁻⁸

The present investigation deals with some reactions of bismuth trichloride using DMF as a medium. Bismuth trichloride is exceedingly soluble in DMF. After removing the solvent under reduced pressure crystals of the bismuth trichloride solvate separate. The solvate has been isolated and has been found to correspond to the 1:1 adduct $\text{BiCl}_3 \cdot \text{HCON}(\text{CH}_3)_2$. It is soluble in DMF. The reactions of bismuth trichloride with silver nitrate, potassium iodide, triethylammonium chloride, diethylammonium chloride, and bases like triethylamine, diethylamine, α -picoline, and pyridine (all in DMF) have been studied. It was expected that with bases a simple base displacement would occur, but it has been observed that a base-catalyzed solvolytic reaction also occurs. This has led to the isolation of compounds containing the anion of dimethylformamide. Whereas with silver nitrate a simple metathetical reaction occurs, with potassium iodide, triethylammonium chloride, and diethylammonium chloride complex formation takes place giving evidence for both six- and four-coordination of bismuth. These reactions also throw light on the mode of ionization of bismuth trichloride in dimethylformamide.

Experimental Section

Purification of Dimethylformamide.—Dimethylformamide (BDH) was fractionally distilled at reduced pressure. It was then kept over anhydrous sodium carbonate (AR) for over 48 hr with occasional shaking. The solvent was decanted off and distilled, and the fraction boiling at $55 \pm 1^\circ$ and 35 mm pressure was collected and stored in blackened glass-stoppered Pyrex

flasks. The specific conductivity of the solvent is found to be $(1-3) \times 10^{-7}$ ohm⁻¹ (at 25°).

Purification of Bases.—The various amines were refluxed with anhydrous barium oxide and kept overnight. The organic bases were decanted off and then distilled over sodium hydroxide beads. The freshly distilled middle fractions were used.

Bismuth Trichloride Adduct with Dimethylformamide.—Freshly sublimed bismuth trichloride (40 g) was dissolved in 200 ml of dimethylformamide. The excess of the solvent was removed under reduced pressure. White crystals of the adduct separated. These were washed with dry carbon tetrachloride and then with dry ether. The ether was finally removed under reduced pressure. The adduct is quite stable and unlike anhydrous bismuth trichloride does not undergo a change in composition even after a few months and can be stored in a ground-glass stoppered flask. The solid melts at $86 \pm 1^\circ$ and is found to correspond to $\text{BiCl}_3 \cdot \text{HCON}(\text{CH}_3)_2$. *Anal.* Calcd: Bi, 53.93; Cl, 27.22; N, 3.61. Found: Bi, 54.42; Cl, 26.96; N, 3.52. Bismuth trichloride in dimethylformamide produces a turbidity even when a small quantity of water is present. This can be used as a test to see if dimethylformamide is free from water.

Conductivity Bridge and Cell.—A TESLA conductivity bridge was used. For measurement of low resistances a Shedlovsky-type cell having a cell constant of 0.756 was used whereas for high resistances a cell containing electrodes of 1.25 cm² separated by 2 mm having a cell constant of 0.12 was employed.

Conductivity Titrations.—Conductometric titrations were performed in the usual manner and the conductance after applying volume corrections was plotted against the molar ratio (titrant/titrated substance).

Isolation of the Solvolyzed Products of Bismuth Trichloride in Dimethylformamide with Triethylamine, Diethylamine, α -Picoline, and Pyridine.—Samples of 20.0 ml of 0.5 M bismuth trichloride were treated with 10 ml of 4 M triethylamine, diethylamine, α -picoline, and pyridine in DMF separately. A white precipitate was obtained in each case. These were allowed to stand for a few hours in well-stoppered 50-ml flasks to reach equilibrium. The supernatant solution was decanted off and the precipitate was centrifuged and washed with dimethylformamide several times. The dimethylformamide adhering to the precipitate was removed by washing with carbon tetrachloride and then with ether. Finally the ether was removed under reduced pressure.

The samples were analyzed for their bismuth, chlorine, and nitrogen contents. The analyses are given in Table I (compounds 1-4).

Samples of 20.0 ml of 0.5 M bismuth trichloride were also treated with 5.0 ml of 1 M triethylamine or diethylamine in DMF separately so that they were mixed in 2:1 molar ratio. A white precipitate was formed in both cases and isolated in the same manner as described above. These were found to correspond to $\text{BiCl}_2[\text{CON}(\text{CH}_3)_2]\text{HCON}(\text{CH}_3)_2$ (compounds 5 and 6, Table I).

Isolation of the Adduct $\text{BiCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$.—Bismuth trichloride (5 g) was treated with 40 ml of pyridine and refluxed for 2 hr. The clear supernatant solution was taken in another flask and the excess of pyridine distilled under reduced pressure. The solid obtained was washed with dry carbon tetrachloride and then with dry ether. The ether was finally removed under reduced pressure. The sample obtained was analyzed and found to contain 37.6% Bi, 19.3% Cl, and 7.4% N. This corresponds to $\text{BiCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$.

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TABLE I

ANALYTICAL DATA OF THE SOLVOLYZED PRODUCTS OF BISMUTH TRICHLORIDE OBTAINED WITH DIFFERENT BASES^a

Compd	% theoretical			% found		
	Bi	Cl	N	Bi	Cl	N
BiCl ₂ [CON(CH ₃) ₂](C ₂ H ₅) ₂ N (1)	46.1	15.7	6.2	46.6	15.8	6.0
BiCl ₂ [CON(CH ₃) ₂](C ₂ H ₅) ₂ NH (2)	49.2	16.7	6.6	49.4	16.9	6.5
BiCl ₂ [CON(CH ₃) ₂]C ₆ H ₇ N (3)	47.0	15.9	6.3	46.6	15.8	6.1
BiCl ₂ [CON(CH ₃) ₂]C ₆ H ₅ N (4)	48.5	16.5	6.5	47.8	16.4	6.7
BiCl ₂ [CON(CH ₃) ₂]HCON(CH ₃) ₂ (5)	49.2	16.7	6.6	49.7	16.6	6.4
BiCl ₂ [CON(CH ₃) ₂]HCON(CH ₃) ₂ (6)	49.2	16.7	6.6	48.8	16.8	6.8

^a The melting points of the above compounds could not be identified as they decompose on heating.

Methods of Analysis.—In the above compounds bismuth was determined by titrating with EDTA in a buffered solution of pH 2–4 using pyrocatechol violet as indicator¹² and chlorine was determined gravimetrically as silver chloride after dissolving the compounds in nitric acid. Nitrogen was determined by the Kjeldahl method.

Results and Discussion

Bismuth Trichloride in DMF. Reactions.—Bismuth trichloride forms a 1:1 adduct with DMF. Its reactions with silver nitrate, potassium iodide, triethylammonium chloride, diethylammonium chloride, and some bases using DMF as a solvent medium are described below. The discussion is based mainly on the evidence derived from conductance measurements.

Reaction with Silver Nitrate.—When bismuth trichloride is treated with silver nitrate solution in DMF, a white precipitate of silver chloride is formed and the bismuth ions remain in solution. The reaction has been followed conductometrically and a sharp break is observed when 3 mol of silver nitrate is added for 1 mol of bismuth trichloride (Figure 1), indicating that all three chloride ions are precipitated with silver nitrate.

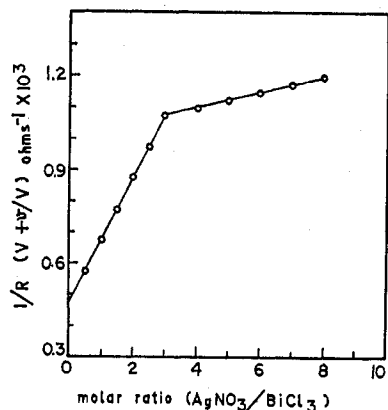


Figure 1.—Conductometric titration of 20 ml of 0.02 M BiCl₃ with 0.4 M AgNO₃ in DMF.

Reaction with Potassium Iodide.—Potassium iodide is soluble in DMF to the extent of about 1 mol/l. Potassium chloride is sparingly soluble in DMF and its solubility has been reported to be 0.05 g/100 g. So, it was expected that when bismuth trichloride would be treated with potassium iodide, a metathetical reaction resulting in the precipitation of potassium chloride should occur. In actual experiment, it has been observed that complex formation reaction takes place rather than the precipitation reaction in the initial stages. When potassium iodide is mixed with bismuth

trichloride in DMF, initially no precipitate of potassium chloride appears but a yellow color develops which gradually deepens to orange and finally to red as the concentration of the iodide is increased. The precipitate of potassium chloride is visible only after 3 mol of potassium iodide for 1 mol of bismuth trichloride has been added. The reaction has been followed conductometrically and three breaks occur, two of these at molar ratios of 1 and 3 indicating the formation of BiCl₂I⁻ and BiCl₃I₃³⁻ (Figure 2). The third break occurs when 4

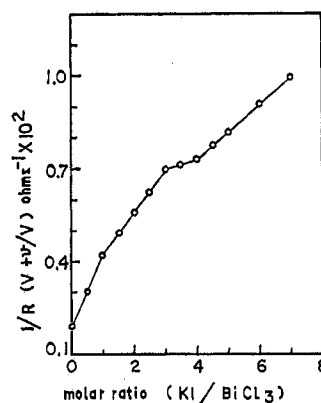
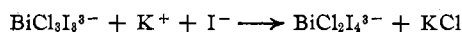


Figure 2.—Conductometric titration of 20 ml of 0.04 M BiCl₃ with 0.8 M KI in DMF.

mol of potassium iodide has been added with simultaneous precipitation of potassium chloride indicating that only one chloride is exchanged with iodide ion in accordance with the equation



Reaction with Triethylammonium Chloride and Diethylammonium Chloride.—The conductometric titration of bismuth trichloride with triethylammonium chloride or diethylammonium chloride shows a break at a 1:1 molar ratio indicating the formation of BiCl₄⁻ ion (Figure 3). The solution remains clear. This is fur-

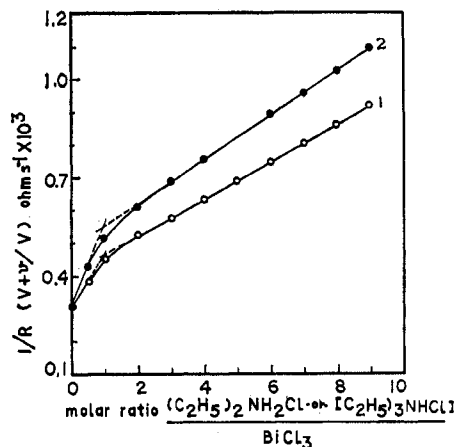


Figure 3.—Conductometric titrations of 20 ml of 0.005 M BiCl₃ with 0.1 M triethylammonium chloride (curve 1) and diethylammonium chloride (curve 2) in DMF.

ther supported by the fact that a solution of bismuth trichloride in DMF dissolves an exactly equimolar quantity of KCl whereas the latter is sparingly soluble in DMF alone.

(12) M. Malat, V. Suk, and O. Ryba, *Chem. Listy*, **48**, 203 (1954); *Collect. Czech. Chem. Commun.*, **19**, 258 (1954).

Reaction with Bases.—When the solution of bismuth trichloride in DMF is treated with bases such as triethylamine, diethylamine, α -picoline, or pyridine a white precipitate or a turbidity is observed. With triethylamine and diethylamine, bismuth is completely precipitated as the supernatant solution is found to be free from bismuth. The presence of the chloride ions in the supernatant solution indicates clearly that a solvolytic reaction takes place. However, with α -picoline and pyridine the precipitation of solvolyzed product of bismuth trichloride is not quantitative even after adding a large excess of the base, and the supernatant solution is found to contain appreciable amounts of bismuth. In order to understand the nature of the above reactions, conductometric titrations of bismuth trichloride with the above-mentioned bases in DMF were carried out. The titrations with triethylamine and diethylamine provide similar curves (curves 1 and 2, Figure 4). The conductivity increases quite sharply

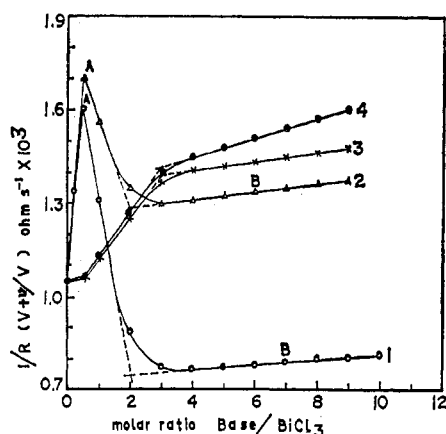
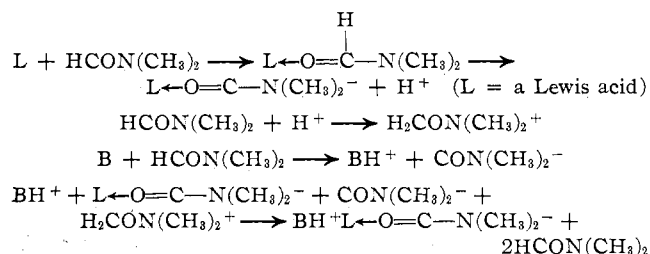


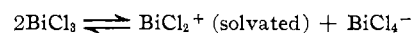
Figure 4.—Conductometric titrations of 20 ml of 0.05 M BiCl_3 with 1.0 M triethylamine (curve 1), diethylamine (curve 2), α -picoline (curve 3), and pyridine (curve 4) all in DMF.

until 0.5 mol of the base for 1 mol of bismuth trichloride has been added and then it sharply decreases giving a peak at a molar ratio of 0.5. Then another break in the curves is seen at a molar ratio of 2.

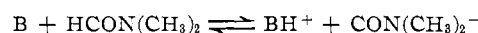
Recently, Paul and coworkers^{10,11} have shown that DMF undergoes autoionization to give $\text{H}_2\text{CON}(\text{CH}_3)_2^+$ and $\text{CON}(\text{CH}_3)_2^-$ ions. They have also explained the polar nature of the solvates formed between Lewis acids and DMF to be due to an ionization process in which the two DMF molecules have been assumed to dissociate into a cation and an anion, and the Lewis acid remains attached to the anion through the oxygen atom.⁹ They have also carried out thermometric titrations of Lewis acids with bases in DMF and have suggested the following reaction sequence to explain the neutralization process



These ideas are, however, unable to explain the above-mentioned reactions of bismuth trichloride with bases. On the other hand, the conductometric titration curves of bismuth trichloride with triethylamine and diethylamine can be readily explained if it is assumed that bismuth trichloride in DMF ionizes in the following way

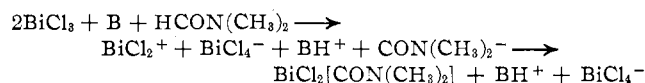


When a base is dissolved in DMF, it would be solvolyzed, the extent of solvolysis depending upon the strength of the base dissolved, and the following equilibrium would exist

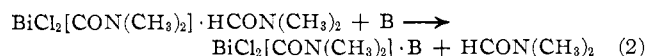
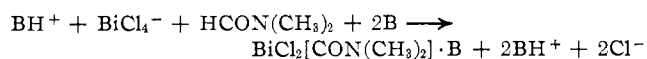
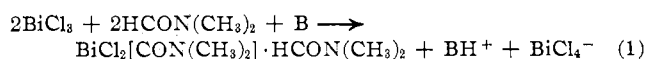


The evidence in favor of the existence of this equilibrium is available from conductance measurements. An increase in the conductance is observed when base is added to DMF or *vice versa*, *i.e.*, under both conditions.

When bismuth trichloride and the base, both in DMF, are mixed together the following reaction may occur



The occurrence of a peak at a molar ratio of 0.5 in the titration curves of bismuth trichloride with tri- and diethylamine supports the above mechanism. The isolated precipitate at this stage corresponds to $\text{BiCl}_2[\text{CON}(\text{CH}_3)_2] \cdot \text{HCON}(\text{CH}_3)_2$ and the increase in conductance at the initial stage may be due to the formation of BH^+ and BiCl_4^- ions. Further, titration results in the decrease of conductance and a second break is observed at a 2:1 molar ratio. The isolated precipitate after adding excess of the base has been found to correspond to $\text{BiCl}_2[\text{CON}(\text{CH}_3)_2] \cdot \text{B}$. This explains the occurrence of the second break at a 2:1 and not at a 1:1 ratio as one would expect. Thus the actual reaction may be represented as



The second stage of the reaction has also been studied conductometrically after preparing $\text{BH}^+\text{BiCl}_4^-$ by an alternative reaction, *i.e.*, by mixing equal volumes of equimolar solutions of di- or triethylammonium chloride with bismuth trichloride in DMF. The mixture was then titrated with di- or triethylamine, respectively (Figure 5). The conductance decreases sharply in the beginning and a break is observed at a 2:1 molar ratio. A precipitate of $\text{BiCl}_2[\text{CON}(\text{CH}_3)_2] \cdot \text{B}$ is formed during the reaction. The curves of these titrations are found to be similar to the portion of the curves (part AB in curves 1 and 2 in Figure 4) representing the stage of the reaction which took place after the addition of 0.5 mol of the base. This not only supports the formation of BiCl_4^- ion in the first stage of the reaction but also indicates that a decrease of conductance would occur during the second stage of the reaction. This has been experimentally verified by measuring the conductance of equimolar solutions (0.1 M) of $[(\text{C}_2\text{H}_5)_2\text{NH}_2]^+\text{Cl}^-$ and

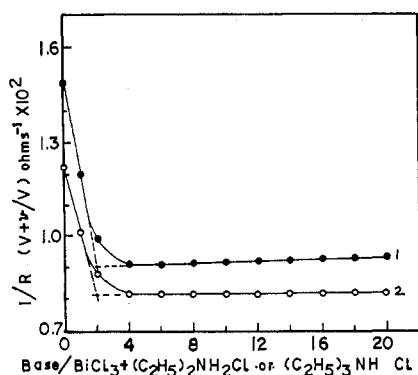


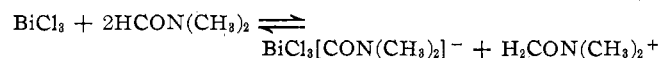
Figure 5.—Conductometric titrations of (i) 10 ml of 0.05 M BiCl_3 + 10 ml of 0.05 M $(\text{C}_2\text{H}_5)_3\text{NHCl}$ with 1.0 M triethylamine (curve 1) and (ii) 10 ml of 0.05 M BiCl_3 + 10 ml of 0.05 M $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Cl}$ with 1.0 M diethylamine (curve 2) in DMF medium.

$[(\text{C}_2\text{H}_5)_2\text{NH}_2]^+\text{BiCl}_4^-$. The specific conductance of the former ($9.32 \times 10^{-4} \text{ ohm}^{-1}$) is considerably less than that of the latter ($2.64 \times 10^{-3} \text{ ohm}^{-1}$).

When the titrations of bismuth trichloride with bases such as α -picoline and pyridine in dimethylformamide are carried out, altogether different curves are obtained (Figure 4, curves 3 and 4). The peaks observed at a molar ratio of 0.5 in the titrations with triethylamine and diethylamine are absent in these curves. However, a small inflection at the 0.5 molar ratio and a clear break at the 3.0 molar ratio can be located in both these curves. Unlike the reaction with triethylamine or diethylamine a heavy precipitate during the titrations is not obtained, but instead a white turbidity appears in both cases. The supernatant solution even after adding several moles of α -picoline or pyridine is found to contain a lot of bismuth. The precipitate which causes turbidity has been isolated and found to be a solvolyzed product corresponding to $\text{BiCl}_2[\text{CON}(\text{CH}_3)_2] \cdot \text{B}$. Since the extent of solvolysis is small with α -picoline and pyridine, a peak is not observed at the 0.5 molar ratio but instead a small inflection at about the 0.5 molar ratio is observed. However, a clear break at the 3.0 molar ratio indicates the formation of $\text{BiCl}_3 \cdot 3\text{B}$, which is probably the main product formed. In order to confirm this view, an adduct of bismuth trichloride with pyridine by direct combination was isolated and found to correspond to $\text{BiCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$. This adduct is soluble in DMF and does not produce the solvolyzed product, *i.e.*, any precipitate or turbidity even after adding a large quantity of pyridine in its dimethylformamide solution. Thus, it seems that with α -picoline and pyridine the main reaction is the formation of $\text{BiCl}_3 \cdot 3\text{B}$ and the solvolytic reaction occurs to a very small extent, and once the bonds between BiCl_3 and the base are established, it is difficult to solvolyze the resulting product. Further, the solvolytic reaction with α -picoline or pyridine is prevented if bismuth

trichloride is previously treated with diethylammonium chloride or triethylammonium chloride. Thus no precipitate or turbidity is observed if α -picoline or pyridine is added to a solution of $(\text{C}_2\text{H}_5)_3\text{NHBiCl}_4$ or $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{BiCl}_4$ in DMF.

Bismuth trichloride is quite a good Lewis acid and the conductivity of its solution in DMF, according to Paul, *et al.*,^{10,11} may be readily accounted for by the existence of the equilibrium



However, it is difficult to explain the following facts on the basis of the above mechanism. (a) A peak occurs in conductometric curves at the 0.5 molar ratio when bismuth trichloride in DMF is titrated with di- or triethylamine. (b) The above equilibrium represents a solvolytic reaction, but it is unable to explain the products of the solvolysis observed in the present studies. (c) The specific conductance of a saturated solution of bismuth trichloride in pyridine (approximately 0.1 M) is appreciable and is of the order of 10^{-3} ohm^{-1} whereas that of the pure solvent is $(4-6) \times 10^{-8} \text{ ohm}^{-1}$. This cannot be accounted for on the basis of a similar equilibrium as it is not possible to assume autoionization of pyridine. On the other hand, the increase in conductance of BiCl_3 in pyridine may be due to the existence of the equilibrium $2\text{BiCl}_3 \cdot 3\text{py} \rightleftharpoons [\text{BiCl}_2(\text{py})_4]^+ + [\text{BiCl}_4(\text{py})_2]^-$. There is no other alternative mechanism by which it could be explained. The existence of $[\text{Bi}(\text{py})_6]^{3+} + [\text{BiCl}_6]^{3-}$ is improbable as highly charged species would not be expected to be formed in a medium of low dielectric constant. (d) On the basis of the above mechanism, a 1:2 solvate of bismuth trichloride with DMF should be formed and not a 1:1 solvate.

These facts indicate clearly that although the above equilibrium may be existing in bismuth trichloride solution in DMF, it occurs to a very small extent and, probably, the main equilibrium which predominates is $2\text{BiCl}_3 \cdot \text{DMF} \rightleftharpoons [\text{BiCl}_2(\text{DMF})_2]^+ + [\text{BiCl}_4]^-$. This explains the above facts as well as the conductivity of bismuth trichloride solution.

It has been observed in the present work that bismuth shows both four- and six-coordination. The steric factor may be one of the reasons for Bi^{3+} favoring four-coordination when DMF or its ions is a ligand, but it is not the only factor. For instance, four-coordination is favored when the Cl^- ion is a ligand whereas six-coordination is favored when the I^- ion is a ligand. This cannot be explained by steric hindrance.

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