

Aluminium Chloride Complexes of 2-Isocyanatobenzoyl Chloride and Phenyl Isocyanate—an Infrared Spectroscopic Study

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The i.r. spectrum of the 1 : 1 complex of aluminium chloride and 2-isocyanatobenzoyl chloride (1), in ethylene dichloride solution has been compared with the spectra of (1)–HCl and PhNCO–AlCl₃ adducts. The (1)–AlCl₃ adduct has been shown to be an equilibrium mixture of at least four structures, namely (1), *N*-dichloroalanylphenylcarbamoyl chloride (11), the insertion compound (12), and the 1 : 2 adduct (14). The formation of *N*-dichloroalanylphenylcarbamoyl chloride in the reaction of aluminium chloride with phenyl isocyanate has been demonstrated. The 1 : 2 adduct of (1)–AlCl₃ has been postulated to exist as an equilibrium mixture of the acyclic compound (14) and the cyclic 1-dichloroalanyl-2-oxo-3,1-benzoxazinium ion (15).

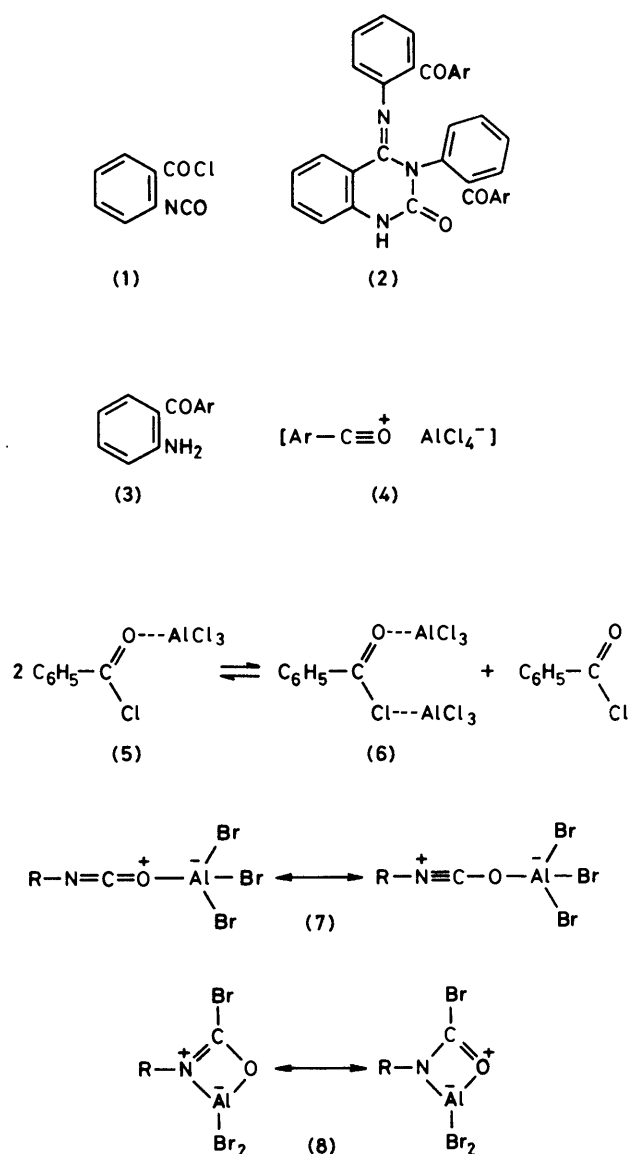
The synthesis¹ of 3-aryl-4-aryliminotetrahydroquinazolin-2-ones (2) from the aluminium chloride complex of 2-isocyanatobenzoyl chloride and the corresponding 2-aminobenzophenones (3) indicated that the (1)–AlCl₃ complex most probably existed as a cyclic derivative. We have now studied the i.r. spectra of the adducts of (1) with aluminium chloride and hydrogen chloride and those of phenyl isocyanate in ethylene dichloride solution and report here our results.

Complexes of aluminium chloride with organic ligands especially acyl halides have been studied¹ because of their importance as intermediates in Friedel–Crafts syntheses. Susz and Cassimatis³ studied the i.r. spectra of the AlCl₃ complexes of 2-methyl-, 2,4-dimethyl-, and 2,4,6-trimethylbenzoyl chlorides in the solid state. Strong absorptions observed at 2200 cm⁻¹ were assigned to the stretching vibration of C≡O⁺ in the ionic complex (4) and the bands near 1540 cm⁻¹ were attributed to CO stretching in the donor–acceptor complex. The benzoyl chloride–aluminium chloride complex however, had bands at 1540 cm⁻¹ and no bands in the triple bond region. Jones and Wood⁴ found $\nu(\text{CO})$ at 1618 cm⁻¹ for the benzoyl chloride–aluminium chloride complex in chloroform solution and assigned the oxonium complex structure (5) co-ordinated *via* oxygen. Corriu *et al.*⁵ supported the oxocarbenium complex but suggested an equilibrium of the 1 : 1 and 1 : 2 adducts (5) and (6) based on the persistence of the 1750 cm⁻¹ band.

Phenyl isocyanate forms⁶ a 1 : 1 complex with aluminium chloride which showed carbonyl absorption at 1650 cm⁻¹ and the structure C₆H₅N=C=O ··· AlCl₃ was assigned. In a later study, Horder and Lappert⁷ isolated the 1 : 1 adducts of aluminium bromide with phenyl and methyl isocyanates as oils. These oils showed bands near 2420 cm⁻¹ and they assigned a metastable co-ordinated complex structure (7) to them. The complexes solidified on standing and their spectra had no bands near 2420 cm⁻¹ but were marked by the appearance of strong absorptions near 1650 cm⁻¹. Horder and Lappert have assigned the insertion structure (8) to the solid complexes because of their monomeric nature in solution.

Results and Discussion

2-Isocyanatobenzoyl chloride (1) was subjected to various ratios of resublimed aluminium chloride in ethylene dichloride and the i.r. spectra of the complexes so formed in solution were recorded immediately. The characteristic absorption maxima are recorded in the Table and the spectra are depicted in Figure 1. 2-Isocyanatobenzoyl chloride (1) gave $\nu(\text{NCO})$ at



2260 and 2295 cm⁻¹ and $\nu(\text{C}=\text{O})$ at 1775 and 1735 cm⁻¹. While the peak at 1775 cm⁻¹ is due to the fundamental stretching mode of C=O of the carbonyl chloride group, the 1735 cm⁻¹ absorption is assigned⁸ to the overtone of the

I.r. absorptions of complexes of 2-isocyanatobenzoyl chloride and phenyl isocyanate with aluminium chloride and hydrogen chloride in ethylene dichloride solution

2-Isocyanato- benzoyl chloride (1) in ethylene dichloride	Absorption frequencies in cm^{-1}						
	(1) : AlCl_3 ratio		(1) : HCl ratio		Phenyl isocyanate in ethylene dichloride	PhNCO : AlCl_3 ratio	
	1 : 1	1 : 2-1 : 2.5-1 : 3	1 : 1	1 : 2		1 : 0.5	1 : 1
	2 770 (br, w)	2 770 (br, w)				2 775 (br, m)	2 775
2 295 (vs)	2 295 (s)		2 285 (s)	2 280 (s)	2 290 (vs)	2 280 (s)	
2 260 (vs)	2 270 (s)		2 260 (s)	2 260 (s)	2 260 (vs)	2 255 (s)	
		1 865 (s)					
		1 830 (m)					
1 775 (s)	1 775 (s)	1 775 (vw)	1 775 (s)	1 765 (s)		1 765 (s)	
1 735 (s)	1 725 (s)	1 730 (vw)	1 715 (m)	1 715 (m)			
	1 670 (w)	1 665 (s)					
	1 640 (w)	1 640 (s)					
1 600 (s)	1 600 (w)		1 600 (m)	1 600 (m)	1 600 (s)	1 640 (m)	1 640 (s)
1 560 (w)	1 580 (m)	1 560 (m)	1 580 (m)	1 580 (m)		1 600 (m)	1 600 (m)
1 500 (w)	1 500 (m)		1 500 (m)	1 500 (m)			
1 200 (s)	1 200 (s)	1 200 (s)	1 200 (s)	1 200 (s)			
1 160 (m)	1 160 (s)		1 160 (s)	1 160 (s)			
1 095 (m)	1 110 (s)	1 085 (br, m)	1 110 (s)	1 110 (s)			

band at 875 cm^{-1} [$\nu(\text{C}-\text{C})$] intensified by Fermi resonance with the fundamental $\text{C}=\text{O}$ stretching vibration.

When 2-isocyanatobenzoyl chloride (1) is complexed with aluminium chloride in a 1 : 1 ratio, the intensity of $\nu(\text{NCO})$ is reduced to nearly half while that at $1 775 \text{ cm}^{-1}$ increased and the $1 735 \text{ cm}^{-1}$ band remained unchanged. In addition, weak absorptions at $1 670$ and $1 640$, medium strong bands at $1 580$ and $1 500$, and strong peaks at $1 160$ and $1 100 \text{ cm}^{-1}$ appeared. Similar observations of the appearance of strong bands at $1 775$, $1 160$, and $1 110 \text{ cm}^{-1}$ and medium absorptions at $1 580$ and $1 500 \text{ cm}^{-1}$ are made for the spectra of 2-isocyanatobenzoyl chloride in the presence of one or two equivalents of hydrogen chloride; however, the weak bands at $1 670$ and $1 640 \text{ cm}^{-1}$ are totally absent (Figure 1).

Thus, we conclude that the isocyanate group is the first to interact with aluminium chloride forming *N*-dichloroalanyl-*o*-chloroformylphenylcarbamoyl chloride, responsible for the increased intensity of the band at $1 770 \text{ cm}^{-1}$.

Earlier workers^{6,7} who studied phenyl isocyanate-Lewis acid complexes, assigned structures (7) and (8) on the basis of i.r. absorptions near $2 400$ and $1 650 \text{ cm}^{-1}$, respectively. In view of the observed increased intensity of the $1 770 \text{ cm}^{-1}$ band in the (1)- AlCl_3 complex, we have re-examined the phenyl isocyanate-aluminium chloride complex to find any possible evidence for i.r. absorption near the $1 750 \text{ cm}^{-1}$ region. When phenyl isocyanate was complexed in ethylene dichloride solution with a one-half equivalent of aluminium chloride, a peak at $1 765 \text{ cm}^{-1}$ appeared with a simultaneous decrease in the intensity of the $\nu(\text{NCO})$ absorption (Figure 2). When one equivalent of aluminium chloride was used, the peak at $2 300 \text{ cm}^{-1}$ disappeared and that at $1 765 \text{ cm}^{-1}$ shifted to $1 640 \text{ cm}^{-1}$. We assign the $1 765 \text{ cm}^{-1}$ band in the PhNCO- AlCl_3 complex to the CO stretching vibration of *N*-dichloroalanyl-*N*-phenylcarbamoyl chloride; chloroformates, chlorothioformates, and dimethylcarbamoyl chloride also absorb in this region.⁹ The absorption at $1 640 \text{ cm}^{-1}$ observed for the 1 : 1 complex is due to the isomerisation of (9) to the cyclic derivative (10), in accord with the observation of Horder and Lappert.⁷

These results coupled with the spectra of 2-isocyanatobenzoyl chloride-hydrogen chloride adduct suggest the

sequence of reactions in the Scheme for the formation of a 1 : 1 complex of (1)- AlCl_3 .

While the increase in the intensity of the $1 775 \text{ cm}^{-1}$ peak is due to the formation of the carbamoyl chloride (11), the weak absorptions at $1 670$ and $1 640 \text{ cm}^{-1}$ are due to small concentrations of (12) and (14). The medium strong band at $1 560 \text{ cm}^{-1}$ is attributed to the perturbed carbonyl vibrations of COCl in (13) and (14) and the displacement is comparable with the shifts observed earlier.³ The existence of free (1) shown by the NCO absorption in the complex supports the formation of species (13) and (14). With hydrogen chloride, although carbamoyl chloride formation occurs, structures of the type (12) and (14) are not possible and hence the peaks at $1 670$ and $1 640 \text{ cm}^{-1}$ are absent.

When the catalyst ratio is raised to 1 : 2, the $\nu(\text{NCO})$ has completely disappeared and a strong peak at $1 865 \text{ cm}^{-1}$ appears. A simultaneous decrease of the $1 775$ and $1 735 \text{ cm}^{-1}$ peaks to very weak absorptions shows that a marked change in the carbonyl chloride group has occurred. The increased intensity of $1 670$ and $1 640 \text{ cm}^{-1}$ bands is obviously due to the increased concentration of the species (12) and (14). The strong absorption at $1 865 \text{ cm}^{-1}$ is due either to a strong-electron withdrawing effect on the carbonyl group or to the ionic species which raise the frequency of CO stretching vibration by increasing the force constant.¹⁰ Thus, the peak at $1 865 \text{ cm}^{-1}$ is assigned to the stretching vibration of $\text{C}=\text{O}$ at C-2 in the 1-dichloroalanyl-2-oxo-3,1-benzoxazinium ion (15).

With a further increase in the ratio of aluminium chloride, no change in the spectrum was observed showing that complexation is complete with 2 equivalents of the Lewis acid. The 1 : 2 adduct of (1)- AlCl_3 is thus shown to be an equilibrium mixture of the cyclic and acyclic derivatives (14) and (15).

Experimental

Purification of Solvent and Reagents.—Ethylene dichloride. Even doubly distilled ethylene dichloride gave a colour with aluminium chloride and to remove the degradable matter present in the solvent, ethylene dichloride (250 ml) was treated with anhydrous aluminium chloride (15 g) and refluxed for 6 h. The brownish suspension was kept overnight and the clear

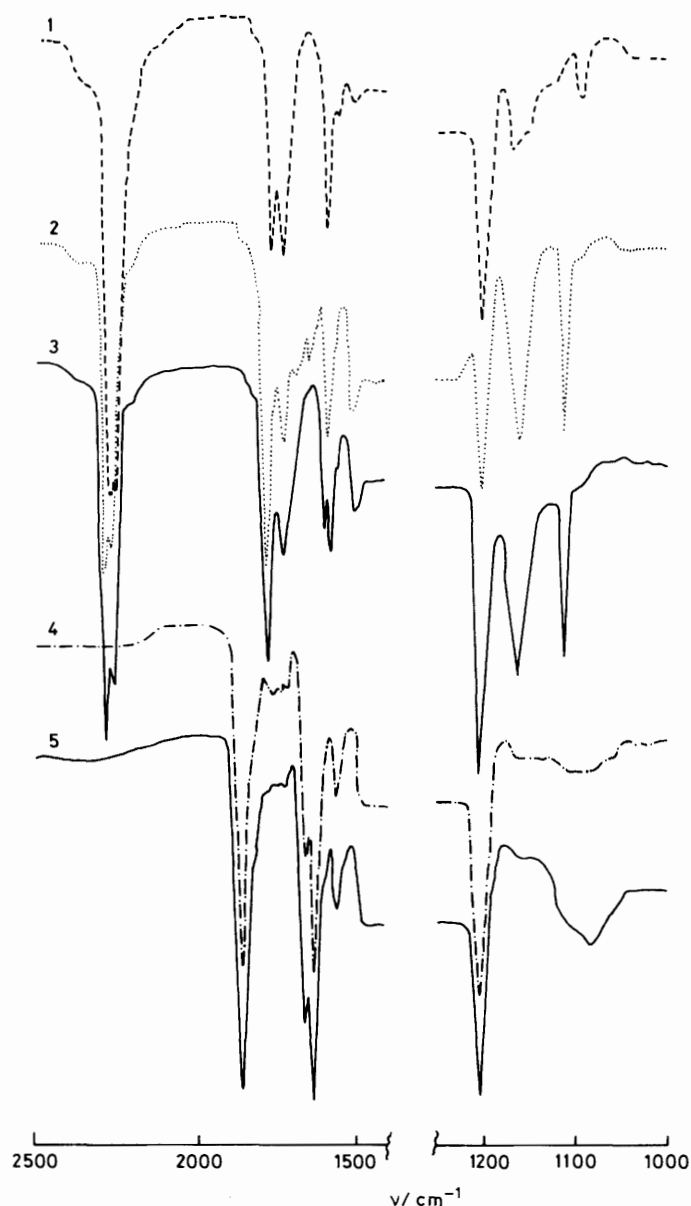


Figure 1. I.r. spectra of AlCl_3 and HCl complexes of 2-isocyanatobenzoyl chloride (1). 1, (1); 2, 1 : 1 (1)- AlCl_3 ; 3, 1 : 2 (1)- HCl ; 4, 1 : 2 (1)- AlCl_3 ; 5, 1 : 3 (1)- AlCl_3

supernatant liquid was decanted off and washed with water (4×50 ml). It was dried (CaCl_2) and distilled; the fraction distilling at $82\text{--}83^\circ$ (150 ml) was refluxed for 1 h with phosphorus pentoxide (8 g) and then distilled under anhydrous conditions. The fraction boiling at $82\text{--}83^\circ$ was collected and stored under nitrogen.

2-Isocyanatobenzoyl chloride. 2-Isocyanatobenzoyl chloride prepared from isatoic anhydride¹¹ when distilled twice under reduced pressure gave a liquid which on standing at 25° solidified as needles, m.p. $30\text{--}31^\circ$, and was stored under nitrogen.

Phenyl isocyanate. Phenyl isocyanate (Fluka) was purified by distillation and the fraction boiling at 55° and 15 mmHg was used.

Aluminium chloride. Reagent grade anhydrous aluminium chloride was powdered and sublimed at 50 mmHg pressure using an apparatus similar to the one used by Cook. The resublimed aluminium chloride was collected in small por-

tions into a number of stoppered test tubes and kept under nitrogen.

Preparation of Complexes.—(1)- AlCl_3 Complexes. A stock solution of 2-isocyanatobenzoyl chloride (0.2989 g) in ethylene dichloride (10 ml) was prepared to furnish a *ca.* 0.0015M solution. Nearly one, two, and three equivalents of aluminium chloride (0.0209, 0.0435, and 0.0639 g) for 1 ml of the above stock solution were weighed, respectively, into three volumetric flasks (10 ml). The exact volume of stock solution required for the Lewis acid taken in the volumetric flasks (0.94, 0.98, and 0.96 ml, respectively) were added and on shaking 20–30 min, aluminium chloride gradually dissolved affording a clear yellow to brownish green solution. The volumes in each of the flasks were made up to 10 ml and the spectra were recorded within 45 min.

(1)-Hydrogen chloride adduct. A slow stream of dry hydrogen chloride was bubbled into dry ethylene dichloride (25 ml) at

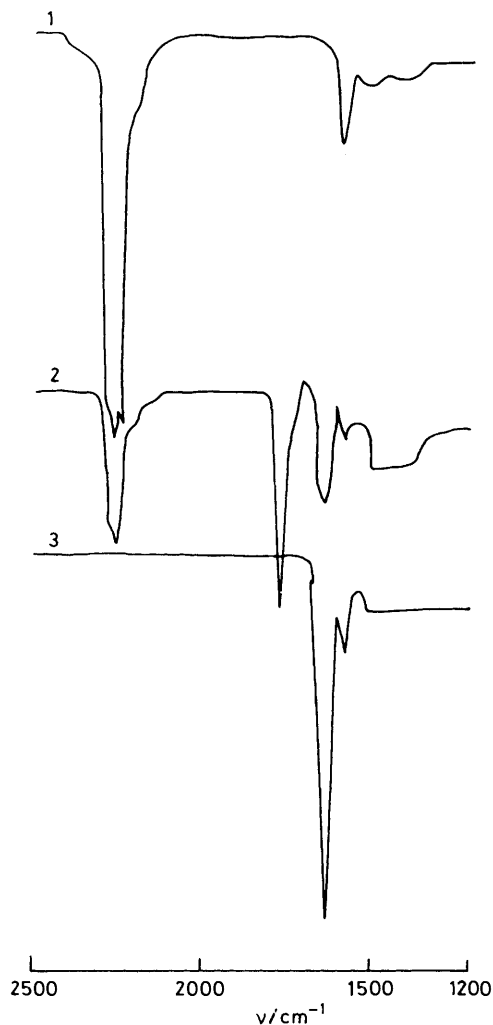
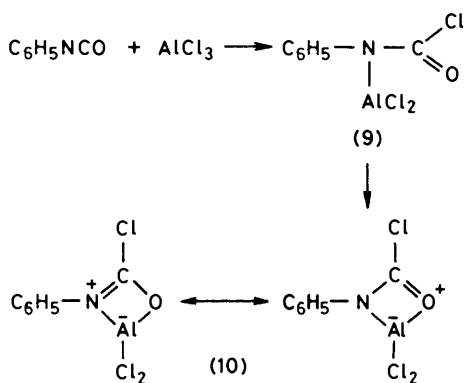
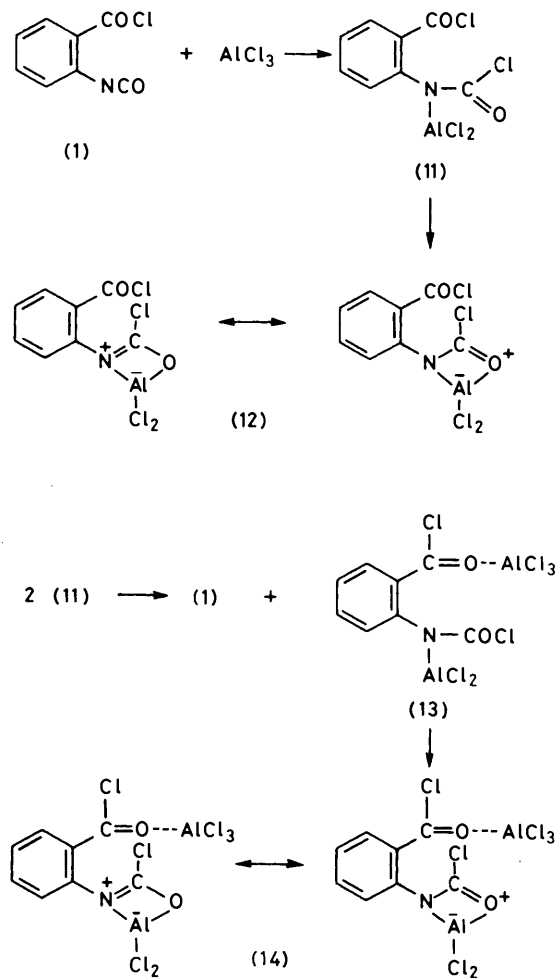


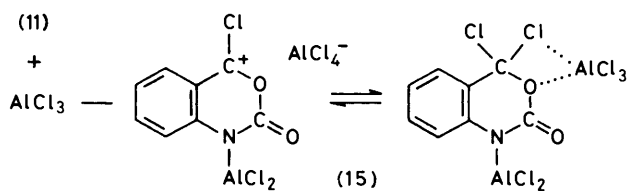
Figure 2. I.r. spectra of AlCl_3 complexes of phenyl isocyanate in ethylene dichloride: 1, phenyl isocyanate; 2, 2:1 phenyl isocyanate- AlCl_3 ; 3, 1:1 phenyl isocyanate- AlCl_3



15° for 30 min. After bringing the solution to room temperature, the amount of hydrogen chloride in the solution was determined by titrimetry and was found to contain 6.253 mg per ml. 1 ml of this solution is equivalent to 31 mg of 2-isocyanatobenzoyl chloride. 1.04 ml each of the stock solution containing 31.05 mg (1), were taken in two volumetric flasks (10 ml). 1 and 2 ml of the hydrogen chloride solution were added respectively to each of the flasks and the volume made



Scheme.



up to 10 ml with ethylene dichloride. The spectra of the resulting solutions were recorded within 10 min of their preparation.

Phenyl isocyanate-aluminium chloride complex. A stock solution of phenyl isocyanate (0.2192 g) in ethylene dichloride (10 ml) was prepared. Approximately one-half and one equivalent of aluminium chloride (0.1350 and 0.2540 g) for 1 ml of the above solution were weighed into two volumetric flasks (10 ml) to which the phenyl isocyanate solution (1 ml) and ethylene dichloride (4 ml) were added. On shaking, aluminium chloride gradually dissolved resulting in a yellow transparent solution. The i.r. spectra of the solutions were recorded within 45 min of their preparation.

Recording of Spectra.—The i.r. spectra of the solutions prepared as above, were recorded at room temperature (*ca.* 27°) on a Perkin-Elmer model 327 grating spectrophotometer using rock salt cells (0.487 mm path length) and ethylene

dichloride as reference. Spectra of pure 2-isocyanatobenzoyl chloride and phenyl isocyanate were taken after diluting the respective stock solutions ten times. Although no change was observed within 3 h of preparation, the i.r. spectrum of the 1:2 complex taken after 15 h at room temperature, had absorptions for both 1:1 and 1:2 complexes indicating partial decomposition.

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