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AN INFRARED STUDY OF HOFMANN- $T_d$ -TYPE CLATHRATES :  
HOST-GUEST INTERACTIONS

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A host-guest interaction in some Hofmann- $T_d$ -type clathrates (general formula :  $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$  where  $M = Zn, Mn, Hg$  and  $Cd$  and  $M' = Cd$  or  $Hg$ ) has been studied using infrared spectroscopy.

An evidence for this interaction is most obvious through the changes of the shape of the bands due to CH out-of-plane bending vibrations originating from the guest (benzene) molecules. Thus, a strong band at around  $700\text{ cm}^{-1}$  appears as doublet at RT as well as at LNT, while the band at around  $980\text{ cm}^{-1}$  splits only at LNT.

The existence of doublets has been explained by the presence of two types of benzene molecules in the unit cell of Hofmann- $T_d$ -type clathrates. Further splitting of these bands (at very low temperatures) is predicted as a result of removal of degeneracy.

#### INTRODUCTION

Hofmann- and Hofmann- $T_d$ -type clathrates represent a part of the class of inclusion compounds in which the guest molecules are accommodated in the host lattice. Their general formula is :  $M(NH_3)_2M'(CN)_4 \cdot 2G$ , where  $M$  is one of the first transition metals, from manganese to zinc, or cadmium,  $M'$  is Ni, Pd or Pt (in Hofmann-type clathrates) and Cd or Hg (in Hofmann- $T_d$ -type clathrates), while  $G$  is usually an organic molecule, such as benzene, aniline, thiophene, etc.

The structure of Hofmann-type host lattice is similar to that of graphite [1] ; it consists of planar layers containing the metal atoms and the cyanide groups, but with the  $NH_3$  groups sticking out above and below the planes. The  $NH_3$



groups then define the voids wherein the guest molecules can be accommodated. Unlike the two-dimensional network observed in Hofmann-type clathrate the lattice of Hofmann- $T_d$ -type has three-dimensional network. The basic difference between Hofmann- and Hofmann- $T_d$ -type clathrates is in the existence of the square-planar  $Ni(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$  or  $Pt(CN)_4^{2-}$  group in the former type and the tetrahedral group, such as  $Cd(CN)_4^{2-}$  or  $Hg(CN)_4^{2-}$  in the later type of clathrates. The main structural difference between Hofmann- $T_d$ -type and Hofmann-type clathrate is that the crystals of Hofmann-type clathrates belong to the tetragonal system, space group  $P4/m$  with  $Z = 1$  [2], while Hofmann- $T_d$ -type clathrates belong to the triclinic, almost tetragonal (pseudotetragonal) system, space group  $P\bar{1}$ ,  $Z = 2$  [3]. Further, in Hofmann- $T_d$ -type, there are two types of cavities, (denoted as I and II in [3]) with different surrounding of the benzene molecules, but both cavities have nearly equal volumes and same framework components. In Hofmann-type clathrates there is only one type of cavity in which the benzene molecules can be enclathrate [2], which has the same framework as cavity I in Hofmann- $T_d$ -type clathrates.

In this type of clathrate, as well as in Hofmann-type, there is no direct chemical bond between the constituents of the host lattice and the enclathrate benzene molecule; the closest contact between them occurs between CH group of the benzene molecules and  $NH_3$  ligands of the host lattice.

In our previous works [4,5], a series of Hofmann-type clathrates (with square-planar  $Ni(CN)_4^{2-}$  group) have been studied using infrared spectroscopy. As a result of these studies, a host-guest interactions have been detected, both in the IR spectra of (i) the benzene (guest) molecules [4] and (ii) the host lattice [5]:

(i) The host-guest interaction in the benzene molecules was detected through the changes of the shape of the band (at around  $980\text{ cm}^{-1}$ ) due to CH out-of-plane bending vibrations. It was found that the magnitude of the splitting of this band at low temperature depends on the volumes of the unit cells and decreases as the volume of the unit cell increases [4].

(ii) A proton-proton interaction, originating from the host-guest interactions in the host lattice, has been proposed to be responsible for the splitting of the infrared bands (detected even at RT) in the region of the symmetric  $NH_3$  bending vibration [5] in Hofmann-type clathrates.

In general, it was suggested that non-bonded proton-proton interactions have a considerable influence on those



types of vibrations in which the motions of the hydrogen atoms are dominant, such as  $\text{NH}_3$  rocking vibration in the host lattice, and CH out-of-plane bending vibrations in the guest molecules.

In this work, we report a host-guest interaction detected through the changes of the shape of the bands due to the  $\gamma(\text{CH})$  bending vibrations in Hofmann- $T_d$ -type clathrates.

### EXPERIMENTAL

The Hofmann- $T_d$ -type clathrates were prepared by similar methods used for preparation of Hofmann-type clathrates [6]. To a mixed aqueous solution (25%) of M(II) chloride salt (in the presence of  $\text{NH}_4\text{Cl}$ ), an equivalent amount of aqueous solution of  $\text{K}_2\text{Cd}(\text{CN})_4$  (or  $\text{K}_2\text{Hg}(\text{CN})_4$ ) was added, pH being around 10. Then an excess of benzene was added, and the resulting mixture was thoroughly mixed with a magnetic stirrer for 1/2 to 1 hr. The precipitate thus formed was filtered out on a glass filter and washed with ethanol. The product was dried in calcium chloride desiccator in the presence of benzene vapour.

The corresponding "empty" clathrates were made in the identical way, except that benzene was not added to the resulting mixture.

The infrared spectra were recorded on Perkin-Elmer 580 spectrophotometer, from KBr pellets and mulls in Nujol. The VLT-2 low temperature cell was used for LNT-IR studies. For precise measurements of the wavenumber, polystyrene film or water vapour was used (resolution at  $1000\text{ cm}^{-1}$  was  $2\text{ cm}^{-1}$ ).

### RESULTS AND DISCUSSION

The infrared spectra of Hofmann- $T_d$ -type clathrate (Cd-Cd-Bz) and its corresponding "empty" clathrate (Cd-Cd) at RT are shown in Fig. 1a. The infrared spectrum of Hofmann-type clathrate (Ni-Cd-Bz) is given for comparison in Fig. 1b. In Table I the absorption bands are listed, and their assignments are given.

There are two main differences in the IR spectra of Hofmann- and Hofmann- $T_d$ -type clathrates and both are related to the CH out-of-plane bending vibrations of the benzene molecules: (a) A strong band at around  $700\text{ cm}^{-1}$ , assigned to the infrared active ( $A_{2U}$ ) CH out-of-plane bending mode [7], appears as a single band in Hofmann-type and as a



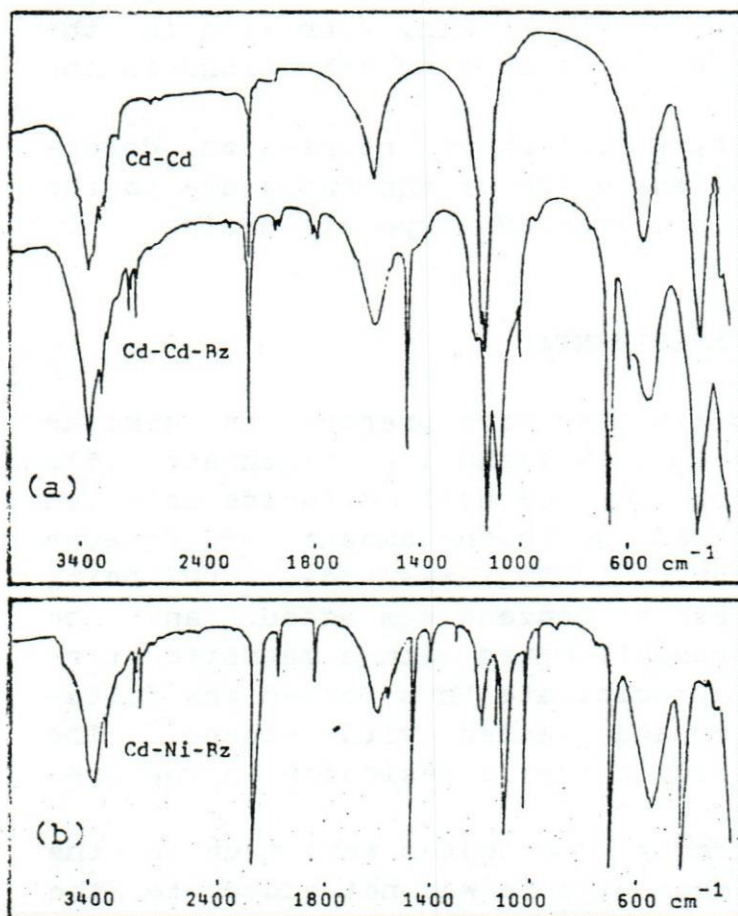


Fig. 1. The IR spectra of Hofmann- $T_d$  (a) and Hofmann-type (b) clathrates at RT. Arrows mark the CH out-of-plane bands.

doublet in Hofmann- $T_d$ -type clathrates. The same behaviour have the two combination bands (due to combinations of at least one CH out-of-plane bending) at around 1985 and 1845  $\text{cm}^{-1}$  (b). The behaviour of a weak band at around 980  $\text{cm}^{-1}$ , assigned as CH out-of-plane bending vibration, having

$E_{2U}$  symmetry [7] is different at LNT in Hofmann- $T_d$ -type compared to Hofmann-type clathrates [4]. We will discuss these points separately.

(a) Doublets at around 700  $\text{cm}^{-1}$  and 1985 and 1845  $\text{cm}^{-1}$  :

The details of these bands in Hofmann- $T_d$ -type clathrates are shown in Fig. 2a and Fig. 2b. The corresponding bands in Hofmann-type clathrates are also given in this figure.

The existence of doublets instead of singlets could probably be explained in terms of different crystal structures between Hofmann- and Hofmann- $T_d$ -type clathrates ; Hofmann-type clathrates have two enclathrate benzene molecules in the unit cell, and only one type of cavity, i.e. only one type of benzene, while Hofmann- $T_d$ -type has four enclathrate benzene molecules and two types of cavities in the unit cell, i.e. at least two types of guest molecules. The guest molecules are relatively remoted from the host lattice; there is no chemical bond between them, and their vibrations can be regarded as "almost free" from the rest of the clathrate. However, the infrared spectra undoubtedly show (Fig. 1 and 2) that the guest molecules are exposed to

Table I. Wavenumbers of the vibrations in "empty" (Cd-Cd) and benzene (Cd-Cd-Bz and Cd-Ni-Bz) clathrates

Cd-Cd	Cd-Cd-Bz	Cd-Ni-Bz	Assignment*
3380 s	3395 s	3380 s, b	
3330 sh			
3290 w	3295 m	3280 w	$\nu(\text{NH}_3)$
3270 w	3240 w		
	3085 w	3075 w	
	3065 w	3055 w	
	3030 w	3025 w	$\nu(\text{CH})$
		3000 w	
2165 s	2170 m	2155 s	
	2160 s	2110 w, sh	$\nu(\text{CN})$
	1985 w	1985 w	
	1970 w		
	1845 w	1845 w	$\text{C}_6\text{H}_6$ combinations
	1830 w		
1600 s, b	1600 s, b	1600 s, b	
		1570 w	$\delta_{\text{as}}(\text{NH}_3)$
	1475 s	1475 s	
		1410 w	$\nu(\text{CC})$
		1310 w	$\delta(\text{CH})$
1175 m, sh	1200 sh	1210 sh	
1155 s	1155 s	1205 s	$\delta_{\text{s}}(\text{NH}_3)$
		1145 m	$\delta(\text{CH})$
	1110 s	1105 s	$2\rho(\text{NH}_3)$
	1030 s	1030 s	$\delta(\text{CH})$
	980 w	985 w	$\gamma(\text{CH})$
	697 s	700 s	$\gamma(\text{CH})$
	685 s		
550 m, b	545 m, b	545 m, b	$\rho(\text{NH}_3)$
335 s	350 s	425 s	$\nu(\text{M-N})$
265 w	265 w		$\delta(\text{N-M-N})$

\* s-strong; m-medium; w-weak; sh-shoulder; b-broad;  $\rho$ -rocking;  $\nu$ -stretching;  $\delta$ -in-plane bending;  $\gamma$ -out-of-plane bending; s-symmetric; as-antisymmetric



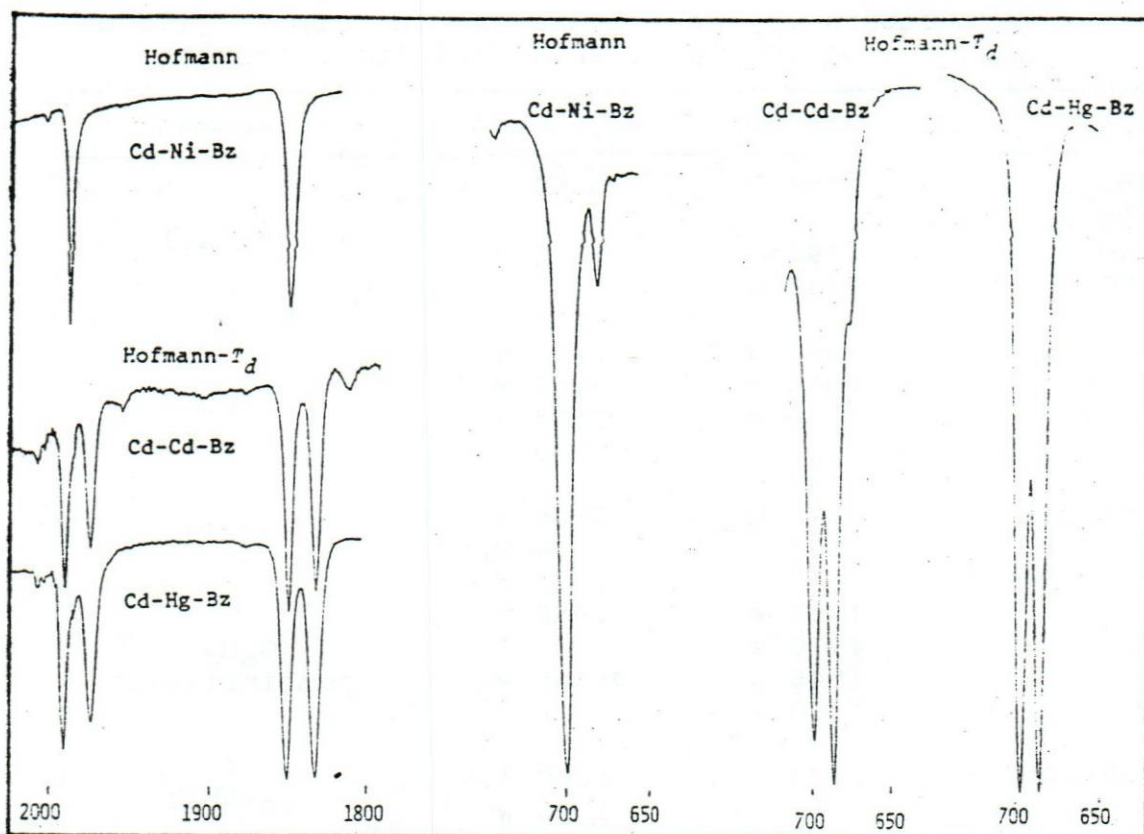


Fig. 2. The details of the IR bands at 1985 and 1845  $\text{cm}^{-1}$  (a) and at 700  $\text{cm}^{-1}$  (b) in Hofmann- and in Hofmann- $T_d$ -type clathrates at LNT

a certain interaction in the host lattice and vice versa. The host-guest interactions are more likely to be present than the guest-guest interactions since the guest molecules are completely enclathrate by the host lattice. It is expected, similarly as in Hofmann-type clathrates, that the nearest distance between the (non-bonded) guest molecules and the host lattice is between the CH groups from the benzene molecules and  $\text{NH}_3$  groups from the host lattice [2]). In view of this, the existence of doublets in the IR spectrum of Hofmann- $T_d$ -type clathrate (Fig. 2) could be explained as a result of different host-guest interactions in cavities I and II. The separation of about 12  $\text{cm}^{-1}$  (at 700  $\text{cm}^{-1}$ ) and about 25  $\text{cm}^{-1}$  (at 1985 and 1845  $\text{cm}^{-1}$ ) suggests that the interactions are stronger in one type of benzene molecules than in the other. Judging from the infrared spectra (Fig. 2a and 2b), one type of benzene, the one in which the interactions are expected to be stronger, is of the same nature as that in Hofmann-type, while in the other, these interactions are probably less strong.

However, it is not immediately clear, why among all pos-



sible motions of the benzene molecule, only bands due to CH out-of-plane bending vibrations exhibit changes, while the others not. The answer for this could be found, again in the existence of host-guest interactions in Hofmann- $T_d$ -type clathrates. It is expected that the CH out-of-plane bending vibrations in the benzene molecule will be influenced by the presence of neighbouring constituents of the host lattice more strongly than the others (say,  $\delta$ CH or C-C-C bendings).

(b) The behaviour of a weak band at around  $980\text{ cm}^{-1}$

In the infrared spectrum of Hofmann- and Hofmann- $T_d$ -type clathrates (Fig. 1) there is another band which can be assigned to the CH bending mode of the benzene molecules: a weak band at around  $980\text{ cm}^{-1}$ , having  $E_{2u}$  symmetry. Although this band is IR and Raman inactive for the free benzene molecule, it can be seen in the IR spectrum of liquid and solid benzene [8], as well as in the infrared spectra of Hofmann-type clathrates [4].

This band has been already studied in Hofmann-type clathrates throughout temperature range from RT to LNT [4]. A splitting of this band at LNT has been detected, the magnitude of which depended on a metal attached to the  $\text{NH}_3$  ligands. It has been proposed that this splitting correlates quite well with the order of decreasing of the unit cell volumes (see Fig. 3 in [4]).

In Hofmann- $T_d$ -type clathrates this behaviour has not clearly been observed. The RT and LNT IR spectra of this band for Zn-Ni-Bz (Hofmann-type) and Zn-Cd-Bz (Hofmann- $T_d$ -type) clathrates are shown on Fig 3. The half-width of this band at RT and at LNT in Hofmann- $T_d$ -type is considerably greater compared to the half-width of the corresponding band in Hofmann-type clathrate [4]. (The half-width of this band in Zn-Ni-Bz is  $5\text{ cm}^{-1}$ , while in Zn-Cd-Bz it is about  $12\text{ cm}^{-1}$ ). In addition to the main maximum, a high frequency shoulder at about  $7-8\text{ cm}^{-1}$

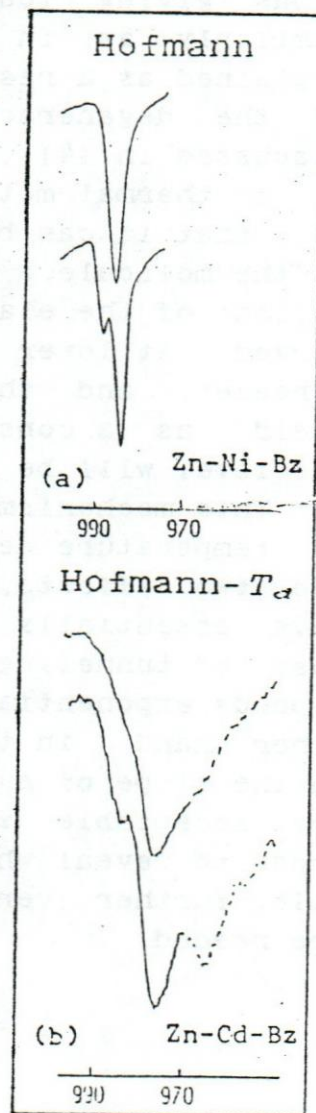


Fig. 3. The details of the weak band at  $980\text{ cm}^{-1}$  in (a) Hofmann- and (b) Hofmann- $T_d$ -type clathrates at RT (upper) and LNT (lower). Dotted lines are nujol bands.



higher frequency appears in Zn-Cd-Bz at LNT (a high frequency shoulder in Zn-Ni-Bz is 3 to 4  $\text{cm}^{-1}$  above the main maximum). This could indicate that the appearance of the high frequency shoulder in Hofmann- $T_d$ -type clathrate at LNT (Fig. 3b) is not of the same nature as the splitting of this band at LNT in Hofmann-type (Fig. 3a), i. e. the removal of the degeneracy [4]. It is more likely that this shoulder in Zn-Cd-Bz originates from the existence of two types of benzene molecules in the unit cell of Hofmann- $T_d$ -type clathrate, the same as it was found as an explanation of the existence of doublets at 700, 1990 and 1850  $\text{cm}^{-1}$ . Considering the widths of these bands, it seems probable that the kind of splitting observed in Zn-Ni-Bz is also present, but can not be resolved (at this temperature in Zn-Cd-Bz the bands are still too wide and are overlapped). Therefore, splitting of both bands at very low temperatures is expected (thus giving four bands, two from each unresolved band) similarly as in Hofmann-type [4]. The splitting could be explained as a result of the mechanisms which lead to removal of the degeneracy, such as tunneling effect (which was discussed in [4]) and hindered rotation.

A thermal motion of the benzene molecules at RT may be such that it can be regarded as "free" rotation in the plane of the molecule. This type of motion leads to an 'isotropisation' of the elastic parameters and the degeneracy is preserved. At lower temperatures, this "free rotation" could 'freeze', and the molecule will vibrate in an anisotropic field, as a consequence of which the double degeneracy of the level will be removed.

This mechanism, as well as tunneling effect, will lead to temperature dependant splitting of the bands. However, the two effects, tunneling effect and hindered rotation, have essentially different temperature dependance. In the case of tunneling effect, the magnitude of the splitting depends exponentially on temperature (eq. 1 in [4]). On the other hand, in the case of hindered rotation a sudden jump in the slope of  $\Delta\nu$  vs.  $T$  may be expected. Both mechanisms are acceptable from physical point of view. However, in order to reveal which of the two mechanisms is more favourable, further (very precise) experiments at low temperatures are needed.



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## POVZETEK

Z infrardežo spektroskopijo smo preučevali medsebojni vpliv host/guest v nekaterih Hofmannovih Td klatratih (splošna formula:  $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ ,  $M = Zn, Mn, Hg, Cd$  ter  $M' = Cd$  ali  $Hg$ ).

Interakcija se kaže v spremembah oblike trakov CH neravninskih nihanj guest molekule - benzena. Tako se močan trak pri približno  $700\text{ cm}^{-1}$  pojavlja kot dublet tako pri sobni temperaturi kakor tudi pri temperaturi tekočega dušika; trak pri približno  $980\text{ cm}^{-1}$  pa je razcepljen le pri nizki temperaturi.

Obstoj dubletov je pojasnjen z dvema zvrstema benzenovih molekul v osnovni celici Hofmannovih Td klatratov. Pričakujemo nadaljnjo cepitev pri zelo nizkih temperaturah kot posledico odprave izrojenosti.

Prejeto:

24.4.1990

Received:

UDK: 543.42:543.7



SECRET

1. The purpose of this document is to provide a comprehensive overview of the current state of the project and to identify the key challenges that must be addressed in order to ensure its successful completion. This document is intended for the use of senior management and other stakeholders who are responsible for the overall direction and funding of the project.

2. The project has made significant progress since its inception, and it is now in a critical phase. The primary objective of the project is to develop a new product that will meet the needs of our customers and provide a competitive advantage for our company. To achieve this objective, it is necessary to address the following key challenges:

3. The first challenge is to ensure that the project is properly managed and that all resources are effectively utilized. This requires a strong project management team that is capable of coordinating the activities of the various departments involved in the project. The second challenge is to ensure that the project is properly funded and that the necessary resources are available to support the project's activities. The third challenge is to ensure that the project is properly communicated and that all stakeholders are kept informed of the project's progress and any changes that may be required.

4. In order to address these challenges, it is necessary to implement a number of key actions. These actions include: (a) establishing a strong project management team; (b) ensuring that the project is properly funded and that the necessary resources are available; and (c) ensuring that the project is properly communicated and that all stakeholders are kept informed. It is also necessary to establish a regular communication schedule and to ensure that all stakeholders are kept informed of the project's progress and any changes that may be required.

5. The project is a complex and demanding task, and it requires the full support and commitment of all stakeholders. It is essential that all stakeholders work together to ensure the project's successful completion and to provide the necessary resources and support to the project team. The project is a key priority for our company, and it is essential that we ensure its successful completion in order to provide a competitive advantage for our company.

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