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DIMETHYL FORMAMIDE SOLVATES OF $CaCl_2$ *

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ABSTRACT

The water of hydration in inorganic salts plays a vital role in stabilising their crystal structures, as is evidenced by the fact that on dehydration the structures change radically. In order to understand further the role played by the solvent in the development of an ordered lattice, dimethyl formamide (DMF) solvates of inorganic salts have been prepared and studied. DMF is a good solvent and has a fairly high dielectric constant. Two compounds, viz. $CaCl_2 \cdot 2.5$ DMF and $CaCl_2 \cdot 2$ DMF, were prepared and were found to be moisture-sensitive. Their thermal stability was determined by micro-thermogravimetry. Both compounds started to lose DMF at 338 K and passed through an intermediate phase, $CaCl_2 \cdot$ DMF, which was stable in the temperature range 408—463 K. However, the differential thermogravimetric run showed four peaks which were also confirmed by differential scanning calorimetry. The X-ray powder diffraction pattern of both the solvates is also presented along with the chemical analysis. A comparative study of their thermal stability is presented.

INTRODUCTION

The water of hydration in inorganic salts plays an important role in stabilising a particular crystal structure. This is evidenced by the fact that on partial or complete removal of the water of hydration, the structure changes radically. In order to understand the role played by the solvent in stabilising a particular structure, we attempted to prepare solvates of inorganic salts with dimethyl formamide (DMF) in place of water. DMF was chosen as solvent because (1) like water, it is stable and can be obtained in pure form, and (2) it has a reasonably high dielectric constant and hence is a polar solvent. DMF is therefore expected to stabilise various structures of solvates of inorganic salts as water does. Steric factors play their own role in the solvates.

In this communication we report the preparation, thermal stability study, differential scanning calorimetric (DSC) runs and X-ray powder patterns of two distinctly crystalline solvates of $CaCl_2$, viz. $CaCl_2 \cdot 2$ DMF and $CaCl_2 \cdot$ 2.5 DMF.

Paul and Sreenathan [1] have reported the formation of DMF solvates of several inorganic salts from their chemical analysis, but they did not report

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any property measurement. The formation of $CaCl_2 \cdot 2\,DMF$ has been reported in the literature [2,3] but details are lacking.

EXPERIMENTAL

The DMF used was B.D.H. LR grade purified by distillation. The TG run of $CaCl_2 \cdot 2\,H_2O$ showed that it dehydrates completely at 425 K and the product $CaCl_2$ is stable up to 1000 K, in agreement with the literature [4]. $CaCl_2$ was prepared by heating the dihydrate in a silica boat at 675 K in a muffle furnace. For the preparation of $CaCl_2 \cdot 2.5\,DMF$, a mixture of 3.9 g of $CaCl_2$ and 6.7 ml of DMF was heated in a closed tube in a water bath at 90°C for 1 h. After cooling back to room temperature, excess unreacted DMF was pumped off under vacuum. $CaCl_2 \cdot 2\,DMF$ was prepared from 1.68 g of $CaCl_2$ and 2.8 ml of DMF. In both cases the product was a white crystalline powder. After powdering well, the product was used for all measurements. Since both compounds were found to be moisture-sensitive, all operations were conducted under a cover of dry N_2 gas and in a glove box.

A micro-TG setup described previously [5], with a sample size of a few mg and a sensitivity of $\pm 50\ \mu g$ was used in flowing N_2 (dry) gas at a flow rate of 10—40 ml min^{-1}.

For the X-ray powder technique, the sample was protected from moisture as described by Kulshreshta [6]. The sample was covered with cellophane tape having a small rectangular window cut in the middle to allow impingement of the X-rays. The window was covered on the inside with a mylar sheet to protect the sample from moisture. The mylar sheet causes little loss in X-ray intensity as compared with cellophane. A commercial Perkin-Elmer DSC 1B with a sample size of a few mg and a heating rate of 8°C min^{-1} was used. Chemical analysis of both solvates for Ca^{2+} and Cl^- content was carried out using standard techniques of EDTA titration and Mohr's method, respectively.

RESULTS

Chemical analysis

The results of the chemical analysis are given in Table 1.

Micro-thermogravimetry

$CaCl_2 \cdot 2.5\,DMF$

The micro-TG run of $CaCl_2 \cdot 2.5\,DMF$ is shown in Fig. 1(a). DMF is lost in two distinct steps: in the first step the loss commences at 323 K and levels off at 420 K; in the second step the loss starts at 475 K and constant weight is attained at 535 K. The relevant details of the micro-TG data of $CaCl_2 \cdot 2.5\,DMF$ are given in Table 2.

TABLE 1

Chemical analysis of $CaCl_2 \cdot 2.5$ DMF and $CaCl_2 \cdot 2$ DMF

Solvates	Formula wt.	% Ca^{2+} content			% Cl content		
		Estd.	Calcd.	Deduced mol. wt.	Estd.	Calcd.	Deduced mol. wt.
$CaCl_2 \cdot 2.5$ DMF	293.4	14.05	13.65	285	23.7	24.2	300
$CaCl_2 \cdot 2$ DMF	256.9	15.52	15.57	257.8	27.1	27.6	261.8

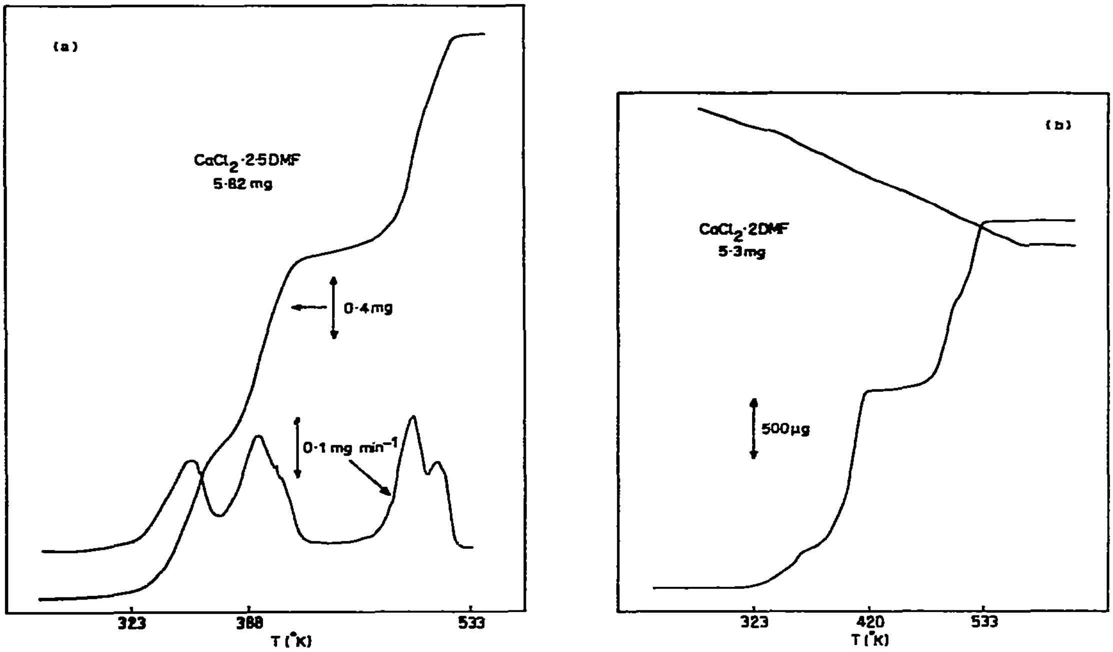

Fig. 1. Micro-TG runs of (a) $CaCl_2 \cdot 2.5$ DMF and (b) $CaCl_2 \cdot 2$ DMF.

TABLE 2

$CaCl_2 \cdot 2.5$ DMF desolvation: micro-TG data

Serial no.	Temp. range (K)	Wt. of starting material (mg)	Observed wt. loss (mg)	Wt. loss in terms of no. of molecules of DMF [a]
1	320—535	5.82	3.64	2.51
2	320—420	5.82	2.22	1.53
3	420—535	5.82	1.40	0.96

[a] Assuming that the residue at $T > 535$ K is totally desolvated $CaCl_2$. This was checked by X-ray.

TABLE 3

$CaCl_2 \cdot 2$ DMF desolvation: micro-TG data

Serial no.	Temp. range (K)	Wt. of starting material (mg)	Observed wt. loss (mg)	Wt. loss in terms of no. of molecules of DMF [a]
1	320—535	5.3	3.0	1.99
2	320—420	5.3	1.6	1.06
3	420—535	5.3	1.4	0.93

[a] Based on the assumption that at $T > 535$ K the residue is $CaCl_2$. This was checked by X-ray.

$CaCl_2 \cdot 2$ DMF

The micro-TG run of this compound is shown in Fig. 1(b). Again, a two-step desolvation is observed. Curiously enough the temperature interval in which the loss of DMF takes place in two steps is very similar in both the solvates. The relevant details of the micro-TG data of $CaCl_2 \cdot 2$ DMF are given in Table 3.

In the micro-TG run of both solvates, after the sample was loaded, dry N_2 gas had to be passed for 2 h to obtain constant weight before commencing a heating run. This indicates that the samples do absorb moisture which can be easily removed.

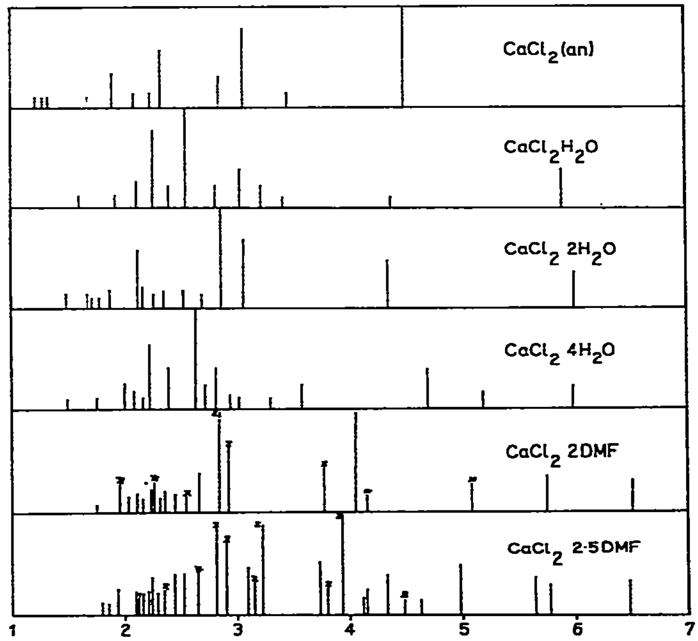

Fig. 2. Room temperature X-ray powder patterns of anhydrous $CaCl_2$ and its various solvates with H_2O and DMF.

X-Ray powder diffraction data

The X-ray powder diffraction data of both the solvates are shown in Fig. 2 along with those of different hydrates of $CaCl_2$ and also anhydrous $CaCl_2$. An important observation is that the relative intensities of some of the reflections are very sensitive to moisture pick-up by the solvates; their intensity changes dramatically with moisture pick-up. However, it is gratifying to note that the original intensities of the moisture-free solvates are restored if the samples are dried over P_2O_5 for 48 h. Thus the moisture absorption is reversible. This is consistent with the micro-TG result before heating.

Differential scanning calorimetry

The DSC scans of both the solvates are given in Fig. 3. Each solvate shows four peaks for desolvation. A DTG run of the $CaCl_2 \cdot 2.5$ DMF is also shown in Fig. 1(a) which indeed shows four peaks. However, in DSC all the peaks are shifted upwards in temperature compared with the DTG peaks. This is understandable because in DTG the sample is heated in flowing N_2 gas so that the liberated DMF is swept off the sample, while in DSC the crimped sample pan does not permit the liberated DMF to leave the sample, thereby developing a back pressure opposing the desolvation. Thus the desolvation

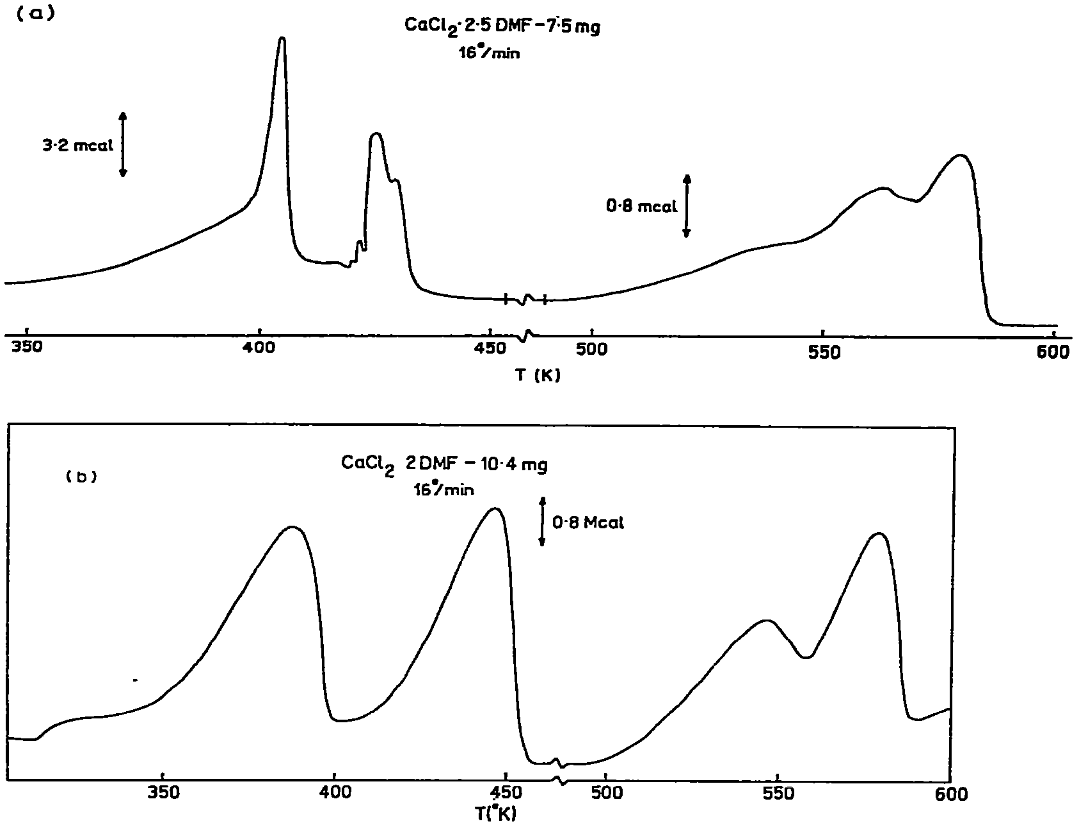

Fig. 3. DSC scans of DMF solvates of $CaCl_2$. (a) $CaCl_2 \cdot 2.5$ DMF and (b) $CaCl_2 \cdot 2$ DMF.

TABLE 4

Desolvation pattern of DMF-solvates of $CaCl_2$

$CaCl_2 \cdot 2.5$ DMF		$CaCl_2 \cdot 2$ DMF	
Temp. of peak in DTG (K)	Calcd. formula of residue	Temp. of inflexion from TG curve (K)	Calcd. formula of residue
363	$CaCl_2 \cdot 1.9$ DMF	363	$CaCl_2 \cdot 1.8$ DMF
398	$CaCl_2 \cdot 1.5$ DMF	404	$CaCl_2 \cdot 1.5$ DMF
501	$CaCl_2 \cdot 0.5$ DMF	506	$CaCl_2 \cdot 0.5$ DMF
521	$CaCl_2 \cdot 0.1$ DMF	525	$CaCl_2 \cdot 0.2$ DMF
538	$CaCl_2 \cdot 0$ DMF	535	$CaCl_2 \cdot 0$ DMF

temperature is enhanced in DSC compared to DTA/DTG. The heats of desolvation of the two steps are: $CaCl_2 \cdot 2.5$ DMF, 31 ± 3 kcal mole^{-1} and 12 ± 2 kcal mole^{-1}; and $CaCl_2 \cdot 2$ DMF, 16 ± 2 kcal mole^{-1} and 12 ± 2 kcal mole^{-1}.

CONCLUSION

From the results it is clear that it is possible to prepare two crystalline solids $CaCl_2 \cdot 2.5$ DMF and $CaCl_2 \cdot 2$ DMF, both of which are moisture-sensitive. Their thermal stability shows that they both desolvate in similar temperature intervals and pass through an intermediate $CaCl_2 \cdot$ DMF. Their X-ray diffraction patterns are similar.

The DTG curve for $CaCl_2 \cdot 2.5$ DMF shows four peaks. The TG run of $CaCl_2 \cdot 2$ DMF shows four points of inflexion. The extent of desolvation of the compounds is calculated corresponding to their peaks/points of inflexion and the corresponding residue composition is calculated. These are shown in Table 4. It is interesting to note that in both the compounds only the first stage is different, viz. $CaCl_2 \cdot 2.5$ DMF and $CaCl_2 \cdot 2$ DMF both pass to the ~1.8 DMF stage and from then on the mode of decomposition is very similar in both the solvates.

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