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$Ca(C_5H_3O_3N_4)_2 \cdot 6H_2O$: A New Hydrate of Calcium Urate

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Calcium urate hexahydrate, $Ca(C_5H_3O_3N_4)_2 \cdot 6H_2O$, has been synthesized for the first time. A tentative assignment of some infrared and Raman bands is given by referring to the isotopic frequency shifts, group frequency considerations, Raman intensities as well as to the spectrum of potassium salt. The spectroscopic data suggest that there are, at least, two types of water molecules in the unit cell. Centrosymmetric unit cell is proposed to explain the spectral features of this compound. X-Ray powder diffraction data are also given. © 1984 Academic Press, Inc.

In connection with a study on the origins of urolithiasis knowledge of the mineral components of renal calculi was needed. Calcium is usually bound to oxalate and phosphate anions (*1–2*) in these biological materials. However, we have found some stones in which calcium, sodium, and urate ions are predominant. We have prepared a new calcium salt of uric acid in order to identify a possible calcium urate in renal calculi. The preparation and some X-ray data of this new urate are reported in this paper. This investigation also presents a tentative vibrational assignment of some bands and proposes a centrosymmetric unit cell to explain the spectral features of this compound.

Experimental

Preparation. This compound was prepared by dropwise addition of calcium hydroxide solution (100 ml, 0.0005 *M*) into a stirring solution (800 ml) containing 0.00125 *M* ($C_5H_4O_3N_4$). This acid is slightly soluble in boiling water, and therefore the reaction temperature must be kept near 100°C. The final solution was concentrated to about 170 ml. After cooling to 15–20°C a precipitate of calcium urate appeared which was filtered and washed with water, ethanol, and diethyl ether. Anal. calcd. for $Ca(C_5H_3O_3N_4)_2 \cdot 6H_2O$: C, 24.89; H, 3.73; N, 23.23; Ca, 8.29; Found: C, 25.05; H, 3.79; N, 23.10; Ca, 8.13

Deuteration of this compound was carried out by using D_2O suspensions which were allowed to stand for 2 hr at 50–60°C. The suspensions were then filtered and the solids dried at 50°C. Deuterium content of samples was determined following the method described in earlier works (*3–4*).

Physical measurements. Infrared spectra were recorded on a Perkin–Elmer 599B spectrophotometer using KBr-pressed disks and Nujol mulls. Raman spectra of the solid, in powder form, were recorded on a Jobin-Yvon U-1000 spectrometer, using the 5145-Å line of a Spectra Physics 164 argon-ion laser as the excitation source.

X-Ray powder diagrams were obtained with a Philips PW 1050 diffractometer using Ni-filtered CuK radiation and a scan speed of 2° (2θ) min^{-1}.

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In the TGA analysis a loss of weight of 22.5% was observed around 130°C with further loss of 57% in the range 350–550°C. Each step caused extensive decomposition. At around 800°C there is another loss of weight of 9%.

Results and Discussion

We have prepared a calcium urate in which the number of water molecules for every calcium ion is 6. The presence of six water molecules is shown by TGA (loss of weight at around 130°C: calculated 22.4%; found, 22.5%). In fact, the infrared spectrum of this compound, upon heating at 200°C, does not show H_2O bending bands in the region 1700–1600 cm^{-1}, but only one band having its absorption maximum at 1595 cm^{-1}. This band is assigned to the urate anion because is also present in the spectra of sodium urate monohydrate upon heating and subsequent loss of the crystallization water molecules. Consequently, the loss of weight occurring around 130°C corresponds to the total content of crystallization water molecules (Fig. 1). Once the releasing of these occurs, the anhydrous salt decomposes at 350–550°C probably follow-

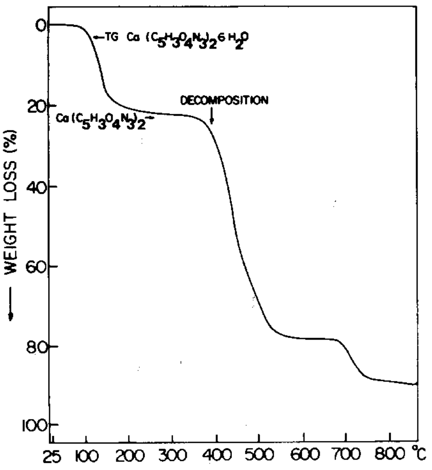

FIG. 1. TG curve of calcium urate hexahydrate.

TABLE I

X-RAY DIFFRACTION DATA OF CALCIUM URATES

d (Å)	I/I_0	d (Å)	I/I_0
	Hexahydrate		
12.26	10	3.161	64
10.77	8	3.015	9
9.50	7	2.846	57
7.13	12	2.744	27
6.10	81	2.575	19
5.90	32	2.520	13
5.71	36	2.486	28
5.40	80	2.330	20
4.50	45	2.225	9
4.22	14	2.101	19
4.02	12	1.815	9
3.863	42	1.773	15
3.720	8	1.654	5
3.558	15	1.604	4
3.360	100	1.571	3
3.229	66		
	Calcium urate[a]		
8.94	14	2.350	16
8.62	28	2.251	16
6.46	27	2.236	20
6.09	48	2.204	5
5.86	64	2.179	6
5.73	22	2.113	4
5.56	24	2.082	4
4.88	45	2.070	4
4.73	8	2.027	4
4.46	9	2.020	4
4.38	14	1.972	8
4.20	3	1.954	10
3.837	47	1.933	5
3.691	18	1.894	9
3.625	25	1.833	5
3.584	2	1.796	5
3.371	2	1.738	5
3.179	75	1.695	3
3.092	100	1.669	3
2.955	27	1.642	2
2.866	32	1.619	4
2.782	35	1.595	4
2.767	34	1.590	4
2.569	15	1.555	6
2.491	8	Plus 12 further reflections up to $2\theta = 100°$	

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[a] From Ref. (6).

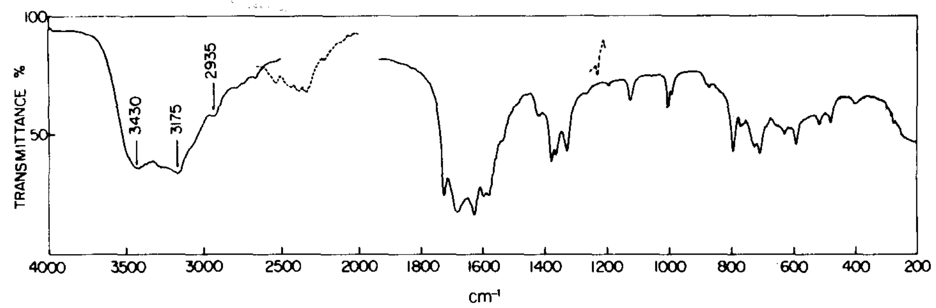

FIG. 2. Infrared spectrum of calcium urate hexahydrate. Dotted line: $\nu(OD)(ND)$ and $\delta(D_2O)$ regions of this compound containing about 18% of deuterium.

ing mechanisms similar to those and anhydrous potassium and sodium urates, which decompose at 330–550°C, respectively (*5*).

The X-ray diffraction pattern of this calcium urate is very characteristic and shows the most intensive line at $d = 3.36$ Å. This pattern (Table I) has not been recorded previously and is different from that of the calcium urate reported in the literature (*6*, *7*).

Comparison of the infrared and Raman spectra (Figs. 2 and 3) of this compound show them to be noncoincident mainly in the region 1750–1450 cm^{-1} (Table II). The hydrogen bonding in this urate is extensive and no doubt the unit cell is centrosymmetric as in the case of sodium urate (*8*), which is the only salt of uric acid whose crystal structure is known. However, centrosymmetric crystals have different space groups, different orientations of related ions or different numbers of equivalent ions in the unit cell. If calcium urate hexahydrate and sodium urate monohydrate possess similar centrosymmetric sheet structures, the anion bands should have similar band locations and relative intensities which is not the case. Therefore, the site symmetry of the urate anion must be different in both salts.

The infrared region 4000–2000 cm^{-1} is complicated because of different hydrogen bonds and correlation field splitting. Furthermore, NH and OH stretching fundamentals and various more or less strong

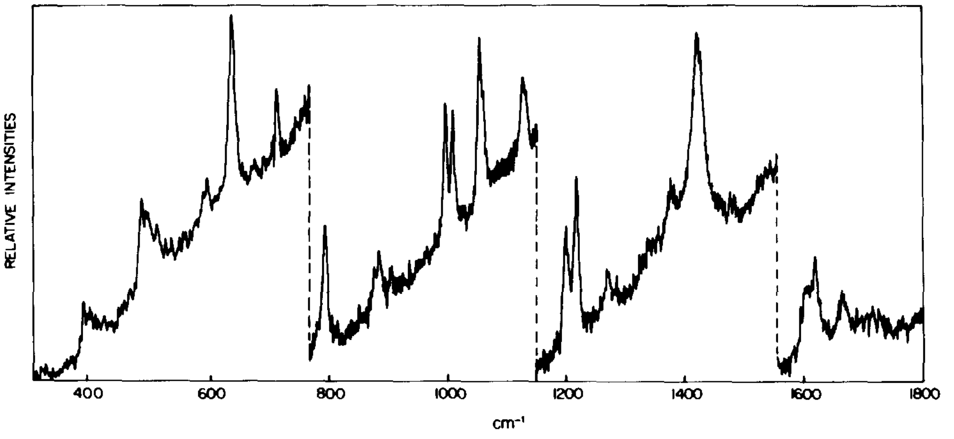

FIG. 3. Raman spectrum of calcium urate hexahydrate.

TABLE II

INFRARED AND RAMAN FREQUENCIES OF CALCIUM AND POTASSIUM URATES

$Ca(C_5H_3O_3N_4)_2 \cdot 6H_2O$			$KC_5H_3O_3N_4$		
Infrared	Raman	Assignment	Infrared	Raman	Assignment
3430 s			2925 s		
3175 s		ν(OH)(NH)	2760 m		ν(NH)
2935 m			2695 m		
1726 s				1667 vw	
					ν(C=O)
	1715 vw		1665 vs		
		ν(C=O),δ(H_2O)			
1686 s				1617 w	
	1666 w		1600 s		
1630 vs			1550 m		
	1618 m		1535 sh		
	1605 m			1436 m	
1600 s			1425 sh		
1581 s				1422 sh	
	1542 vw		1395 s		
1536 sh				1373 vw	
	1480 vw		1365 m		
1421 w	1421 vs			1353 vw	
1380 m			1350 m		
	1377 w		1280 w		
1364 m				1277 vw	
1332 m				1215 s	
1270 vw			1208 vw		
	1267 w			1143 w	
	1216 s		1140 w		
1202 vw				1067 s	
	1198 m		1010 w		
1131 m				1008 s	
	1125 m			883 m	
	1050 s		882 w		
1009 m			820 sh		
	1007 m			799 m	
998 m			795 m		
	995 m		770 m		
	882 w			754 vw	
878 vw			743 w		
797 m			720 w		
	794 m			674 vw	
776 w				632 vs	Purine ring
	703 m		630 vw		Purine ring
732 m			598 m		
714 m				586 m	
690 sh		Librations H_2O	525 m		
662 w		Librations H_2O		509 sh	
636 w		Purine ring		489 m	
	634 vs	Purine ring	483 w		Purine ring
592 m			418 vw		Purine ring
	591 w			393 w	

TABLE II—*Continued*

$Ca(C_5H_3O_3N_4)_2 \cdot 6H_2O$			$KC_5H_3O_3N_4$		
Infrared	Raman	Assignment	Infrared	Raman	Assignment
521 w			300 w		
	509 vw			294 sh	
487 m		Purine ring		275 w	
	482 m				
407 w		Purine ring			
	387 w				

combination and overtones may occur in the same region. The deuterated derivatives should thus be used in order to assign the NH and OH fundamentals correctly. The isotopic dilution studies are particularly useful since they eliminate the intra- and intermolecular coupling and the presence of different bands in such spectra implies different hydrogen bonds. The infrared spectrum of this compound containing about 18% of deuterium (Fig. 2) shows three groups of bands containing some structure, two centered at about 2535 and 2340 cm^{-1}, and the other near 2230 cm^{-1}. These probably correspond to the maxima of the bands centered at 3430, 3175, and 2935 cm^{-1}. The presence of subbands is likely to be due to combinations which become more intense in the case of stronger hydrogen bonds. Consequently, and according to several relations between ν_{AH} frequencies and A . . . B distances (*9*, *10*), we prefer to assign every group of bands to an "average" hydrogen bond (3.15, 2.90, and 2.80 Å in case that the three band groups correspond to N–H · · · O hydrogen bonds, or 2.90, 2.70, and 2.65 Å if these were of the O–H · · · O type).

The exact location of the H_2O deformation band is not known in the infrared range 1700–1600 cm^{-1} because this band is overlapped by other modes involving NH in-plane deformation. However, the former shifts usually to the region 1235–1200 cm^{-1} (*4*) upon deuteration and it can be easily assigned in the spectrum of this urate if there was no deuterated anion band in this spectral range. Potassium urate which is anhydrous, shows no band in this frequency interval upon deuteration. On this basis, we assign the 1216-cm^{-1} infrared band of calcium urate hexahydrate to the D_2O deformation mode. The fact that, in the spectrum of the deuterated compound, only one D_2O deformation frequency appears suggests that only one H_2O deformation frequency exists too. Therefore, one could suggest the existence of only one type of water molecules in the unit cell. However, an assignment of $\nu(OH)(OD)$ and $\delta(HOD)$ modes in needed to assert it, because sometimes only one D_2O deformation frequency appears despite the differences in the geometry and environment of several types of water molecules (*11*). Unfortunately, we cannot assign these bands in this compound because of their overlapping with those of the NH groups. On the other hand, several water bands, which are sensitive to deuteration, are absent in the spectra of potassium salt (Table II). Thus, a weak band at 662 cm^{-1} and a shoulder at around 690 cm^{-1} are characterized as due to water librations. It is, however, difficult to decide which librational mode (rocking, wagging, or, possibly, twisting) is responsible for this pair of bands (the appearance of two bands corresponding to a given mode suggests, of course, the existence of two types of water molecules in the unit cell).

Between 1600 and 300 cm^{-1}, the spectra of deuterated and nondeuterated hydrate differ both in number and relative intensity of the bands. The difference is due mainly to the fact that many of the vibrations in this region are coupled with the NH (ND) deformation bands as reported in other papers for uric acid (*12*). Upon deuteration the 636-, 487-, and 407-cm^{-1} infrared bands remain with approximately the same intensity distribution and frequencies. The same can be said for the corresponding bands of potassium urate at 630, 483, and 418 cm^{-1}. This fact suggests strongly that these bands should be attributed to pure ring vibrations. On the other hand, some Raman bands of this calcium urate may be compared to corresponding ones in the uric acid spectra. This is particularly the case for the strong calcium urate Raman band at 634 cm^{-1} and the strong 625-cm^{-1} uric acid Raman band which could be attributed to ring-breathing vibration.

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