

SHORT COMMUNICATIONS

VIBRATIONAL SPECTRA OF $Mg_2P_4O_{12}$

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THE infrared and Raman spectra of tetrametaphosphates of divalent metals have been reported earlier¹⁻⁴. It was found that the symmetry of the anion (P_4O_{12}) is different in different crystals— C_{2h} in $Zn_2P_4O_{12}$, S_4 in $Co_2P_4O_{12}$ and D_{2d} in $Cu_2P_4O_{12}$. However, in $M_2P_4O_{12}$ ($M=Fe, Ni$) the anion is found to have C_i symmetry, which is in agreement with X-ray results. The vibrational-spectral analysis of a similar compound is reported here.

The Raman spectrum was recorded using a SPEX 'Ramalog' 1401 double monochromator with the finely powdered sample taken in a capillary tube. The 4880 Å line of a Spectra Physics model 165 argon ion laser was the excitation. The IR spectrum was obtained on a PE 225 spectrometer with the sample as Nujol mull.

$Mg_2P_4O_{12}$ crystallizes in the monoclinic system with space group^{5,6} C_{2h} . There are four formula units in the crystallographic unit cell⁵. Since the crystallographic unit cell is not primitive, the number of molecules per Bravais unit cell is considered (which is 2 here). Of the 108 vibrations predicted, 51 modes are Raman-active ($25 A_g + 26 B_g$) and 54 modes are IR-active ($27 A_u + 27 B_u$). The remaining 3 modes ($A_u + 2 B_u$) are acoustical vibrations.

The free ion model predicts 42 modes of internal vibrations. Since more than 42 bands are observed, a factor group model has been used to interpret the spectrum. The interpretation was done on the same basis as for the other tetrametaphosphates reported earlier³.

The presence of coincidences between the IR and Raman lines in the spectra rules out the possibility of a centre of symmetry for the anion, which eliminates the free ion symmetries C_i and C_{2h} out of the four possible symmetries predicted (C_i, C_{2h}, S_4 and D_{2d}). A comparison of the spectra with those of

$Cu_2P_4O_{12}$, reported earlier³, shows that the symmetry of the anion in $Mg_2P_4O_{12}$ is lower than that in $Cu_2P_4O_{12}$. For instance the asymmetric POP stretching mode splits into four components in

Table 1 Assignment of the fundamental vibrations in $Mg_2P_4O_{12}$ and $Cu_2P_4O_{12}$

$Mg_2P_4O_{12}$		$Cu_2P_4O_{12}$		Assignment
Raman	IR	Raman	IR	
1365 vw	1340 s	1338 w	1270 w	$\nu_{asy}(PO_2)$
1349 vw	1295 s	1294 s		
1326 s		1263 vs		
1289 s				$\nu_{sy}(PO_2)$
1168 vs		1170 vs	1130 w	
1139 w		1145 vs		
1120 vw		1088 m		
1059 w		1062 m		
		1061 m		$\nu_{asy}(POP)$
1049 vw	1045 s	930 w		
1009 w				
972 w				$\nu_s(POP)$
910 vw				
822 w	742 vs	812 w	730 vs	
798 vw	719 vs	811 w		
765 vw		690 vs		
689 vs				$\delta(PO_2)$
618 m	592 m	626 s	580 w	
553 w	560 m	525 m	560 w	
510 vw	532 m	524 m	524 w	
462 w	516 s	462 vw	490 m	
446 w	470 w	441 m	462 w	$\delta(POP) +$ M-O stretching
			448 w	
418 vs	416 s	409 vs	398 m	
390 vw	393 s	387 vs	360 w	
360 vs	358 w	360 vw	330 m	
				Lattice modes
340 m	338 w	350 s	300 vw	
324 vw	323 s	325 w	275 m	
298 vw	293 s	285 w	245 ms	
249 m	258 w	272 m	219 m	
224 w	240 m	240 w		
196 m	218 w	220 m		
173 w		207 m		
		158 w		
		157 w		
144 w		106 w		
102 m		85 m		
72 w		68 m		
60 vw				

vw, Very weak; w, Weak; m, Medium; s, Strong; vs, Very strong.

$Mg_2P_4O_{12}$, whereas only one line is observed in $Cu_2P_4O_{12}$ (in Raman). Similar splittings are observed in the other regions also. The characteristic IR absorption line of a cyclic P_4O_{12} ion (symmetric POP stretching) is observed as a doublet at 742 and 719 cm^{-1} in $Mg_2P_4O_{12}$, whereas only one line is observed for $Cu_2P_4O_{12}$ (at 730 cm^{-1}). The complete assignment of the observed frequencies is given in table 1. The frequencies of $Cu_2P_4O_{12}$ are also given in table 1 for comparison.

The splitting of different modes into several components indicates that the symmetry of the anion in $Mg_2P_4O_{12}$ is lower than that in $Cu_2P_4O_{12}$ which has D_{2d} symmetry. Thus it can be concluded that the symmetry of the P_4O_{12} ion in $Mg_2P_4O_{12}$ is S_4 .

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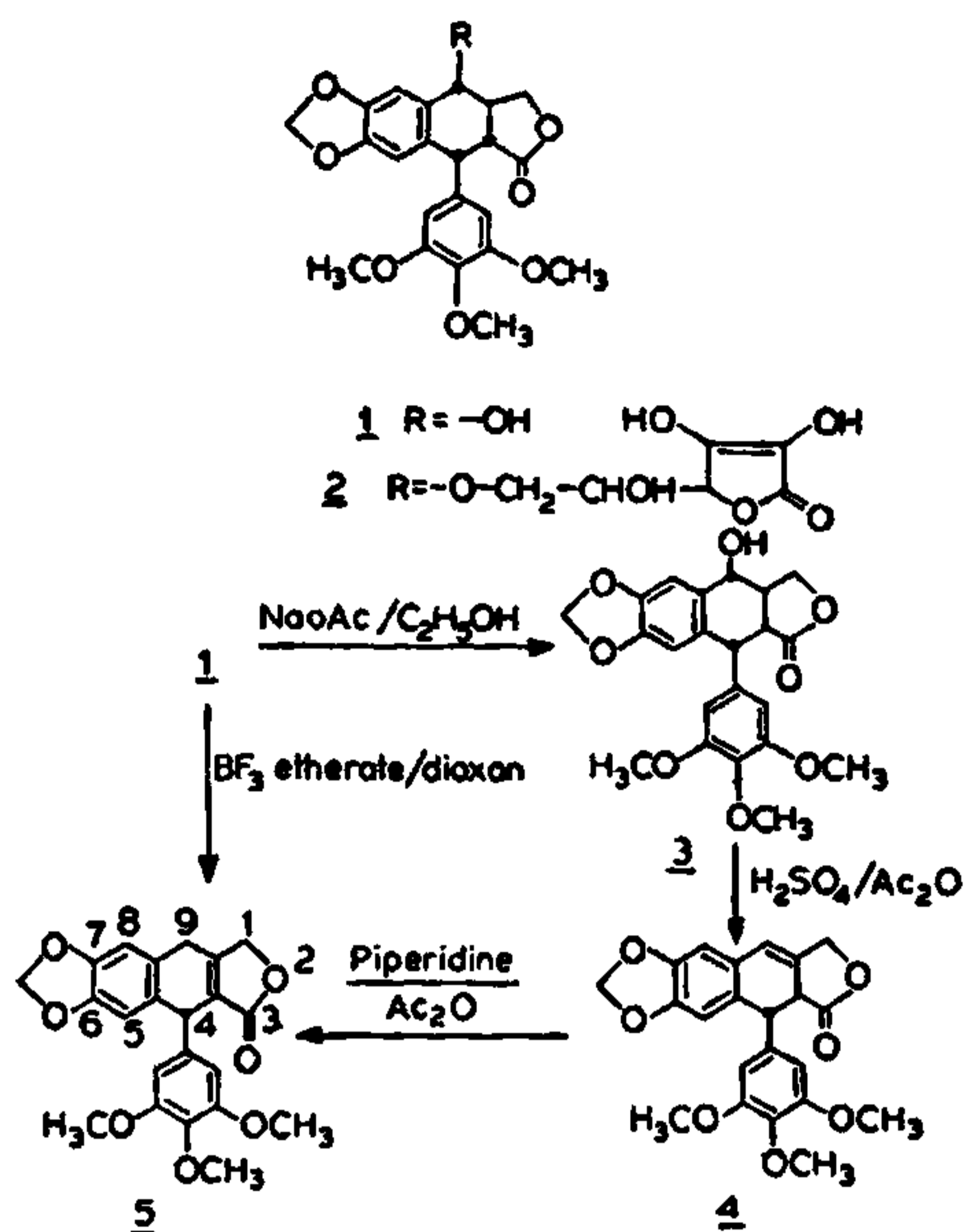
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A NEW ONE-STEP PREPARATION OF β -APOPICROPODOPHYLLIN FROM PODOPHYLLOTOXIN

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BETA-apopicropodophyllin was prepared in one-step in excellent yield by dehydration of podophyllotoxin (1) with boron trifluoride etherate in dioxan.

Podophyllotoxin (1) and several of its analogues and derivatives are cytostatic spindle poisons¹ and



antitumour agents, some at clinical level². 1 contains a *trans* fused highly strained γ -lactone system³, a feature that correlates with epimerization of 1 to its thermodynamically stable *cis* epimer picropodophyllin(3)⁴. β -Apopicropodophyllin (5), a dehydration product of 1, contains a *cis*-fused lactone system and acts as a much stronger antimitotic agent⁵; 5 was prepared previously by a three-step procedure⁶ (starting from 1 involving epimerization of 1 to 3, dehydration of 3 to α -apopicropodophyllin (4) and base-catalysed isomerization of 4 to 5) and also by a single-step procedure using *p*-toluenesulphonyl chloride and pyridine⁷.

As reported earlier⁵ some of the ether derivatives of 1 were more biologically active than 1. It was envisaged that incorporating ascorbic acid in 1 through an ether linkage as in 2 might enhance the biological activity and therefore we decided to prepare the compound 2.

On stirring a mixture of 1 and ascorbic acid in the presence of borontrifluoride etherate in dioxan at room temperature and follow-up of the reaction, it was found that β -apopicropodophyllin (5) was the major product. When a mixture of 1 and ascorbic acid in dioxan was stirred no new product was obtained while only borontrifluoride etherate effected the dehydration of 1 with concomitant isomerization