Journal of Organometallic Chemistry, 54 (1973) 341–344
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VIBRATIONAL SPECTRA OF PHENYLETHYNYLCOPPER(I)

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(Received September 19th, 1972)

SUMMARY

The infrared and laser Raman spectra of phenylethynylcopper(I) (CuPE) have been recorded and the assignment of several bands in the spectra is given. The spectral data obtained do not support the presence of two different types of C≡C bonds in the structure of CuPE as previously suggested by X-ray analysis.

INTRODUCTION

In recent years, copper(I) acetylides have been increasingly employed in organometallic syntheses[1] where it is desired to introduce ethynyl radicals with various substituents into organic molecules. The particular structure of copper(I) acetylides which are π–σ complexes seems to provide the main reason for their photosemiconductor properties[2]. However detailed investigations of the structures of substituted copper(I) acetylides have to date not been reported and spectral studies have been limited to the ν(C≡C) region of the spectrum[3]. We are at present undertaking a systematic study of the vibrational spectra of various copper(I) organoacetylides and this report deals with the results obtained for phenylethynylcopper (CuPE).

X-ray data[4] suggest that this complex possesses a polymeric structure, the distance between the Cu atoms being less than the sum of their covalent radii. The C atoms are externally linked with the Ph–C≡C– ligands both by π and σ bonds. Apparently, two different types of Ph–C≡C– groups exist in this structure[4], the lengths of the C≡C bonds being 1.33 and 1.24 Å respectively.

EXPERIMENTAL

The IR spectra of CuPE over the range 4000–250 cm^{-1} were recorded using UR-20, Perkin–Elmer 457 and Hitachi–Perkin–Elmer 225 spectrophotometers with KBr pellets or Nujol mulls. The Raman spectra were obtained using Coderg-PHO and modified DFS-type instruments equipped with He/Ne lasers.

RESULTS

The results for CuPE are presented in Table 1 where the data for "free" PhC≡CH are also given for comparison. The assignment of fundamental frequencies

TABLE 1

VIBRATIONAL SPECTRA OF PhC≡CH AND PhC≡CCu

PhC≡CH				*PhC≡CCu*	
Raman(liq.)		*IR(liq.)* $\nu(cm^{-1})$	*Assignment*[a]	*Raman(solid)* $\Delta\nu(cm^{-1})$	*IR(solid)* $\nu(cm^{-1})$
$\Delta\nu(cm^{-1})$	ρ				
162 m	0.75		ν_{24} ν(C–C≡C)	150 m	
				200 m	
					286 s
				308 m	
353 m	0.61	352 s	ν_{36} β(C–CCH)		366 s
			ν_{23} γ(C–CCH)		
		418 vw	ν_{16} ϕ(C–C)		403 w
				422 vs	424 w
466 w	0.19	465 vw	ν_{13} α(C–C–C)		
514 w	0.67	513 w	ν_{35} β(C–C≡C)	515 m	515 s
530 m	0.69	530 s	ν_{22} ϕ(C–C)	529 vs	525 s
621 w	0.76	623 s	ν_{34} α(C–C–C)	623 w	623 w
			ν_{21} γ(C≡C–H)		
		655 s	ν_{33} β(C≡C–H)		
		690 vs	ν_{20} ϕ(C–C)	685 w	685 s
		756 vs	ν_{19} γ(C–H)	749 m	746 vs
760 m	0.12		ν_{12} α(C–C–C)		
				780 s	779 w
		842 vw	ν_{15} γ(C–H)		840 w
		916 s	ν_{18} γ(C–H)		915 m
		968 vw	ν_{14} γ(C–H)		960 m
985 w (sh)		985 vw	ν_{17} γ(C–H)		980 m
998 vs	0.10	994 vw	ν_{11} ring breathing	999 m	999 vw
1024 w	0.00	1025 s	ν_{10} β(C–H)		1026 m
1062 w	0.10		$2\nu_{22}$		
		1070 m	ν_{32} β(C–H)		1070 m
1157 w	0.72	1157 w	ν_{31} β(C–H)	1157 vw	1156 m
1175 m	0.20	1175 w	ν_{9} β(C–H)	1172 w	1173 w
1192 s	0.30	1192 vw	ν_{8} ν(C–CCH)	1192 m	1191 w
		1282 w	ν_{30} β(C–H)		1280 w
		1310 vw	$2\nu_{33}$		
1327 vw		1330 w	ν_{29} ν(C–C)		1328 vw
					1380 w
1440 w		1443 s	ν_{28} ν(C–C)		1440 m
1485 w	0.60	1487 s	ν_{7} ν(C–C)	1483 vw	1481 m
		1573 m	ν_{27} ν(C–C)		1571 m
1597 s	0.53	1597 m	ν_{6} ν(C–C)	1594 m	1594 m
		1674 w	$\nu_{18}+\nu_{19}$		1660 w
		1755 w	$\nu_{15}+\nu_{18}$		1747 w
		1806 w	$\nu_{14}+\nu_{15}$		1805 w
		1883 w	$\nu_{14}+\nu_{18}$		1880 w
1948 w		1952 w	$\nu_{14}+\nu_{17}$	1926 s	1930 m
		1970 vw	$2\nu_{17}$	1971 m	
2060 w			$2\nu_{10}$		

(*continued*)

TABLE I (*contd.*)

PhC≡CH				*PhC≡CCu*	
Raman(liq.)		*IR(liq.)* $\nu(cm^{-1})$	*Assignment*[a]	*Raman(solid)* $\Delta\nu(cm^{-1})$	*IR(solid)* $\nu(cm^{-1})$
$\Delta\nu(cm^{-1})$	ρ				
2107 s	0.23	2112 m	ν_5 $\nu(C{\equiv}C)$		
2554 w	0.00		$2\nu_{30}$		2470 w
					2626 vw
2967 w		2970 vw	$2\nu_7$		2960 vw
		3023 w	$\nu_{27}+\nu_{28}$		3016 w
		3036	ν_4 $\nu(C{-}H)$		3029 w
3058 w		3060 w	ν_{26} $\nu(C{-}H)$	3060 vw	3065 w
3067 s	0.16	3067 m	ν_3 $\nu(C{-}H)$		3079 w
		3083	ν_2 $\nu(C{-}H)$		
		3100 w	ν_{25} $\nu(C{-}H)$		3098 vw
3145 w	0.51	3150 vw	$2\nu_6$		3140 vw
3290 m	0.00	3292 vs	ν_1 $\nu(C{\equiv}C{-}H)$		

[a] See ref. 5.

for PhC≡CH was recently suggested by King and So[5]. The analysis of the data presented lead to the following conclusions.

(*i*). The frequencies due to the ligand vibrations in the spectral region 1600–800 cm^{-1} are essentially the same as in the spectrum of the coordinated ligand with their values being similar to within a few cm^{-1}. The main differences occur in the low frequency region of the spectrum where, in addition to a shift of the ligand bands, several new bands appear which are very strong in the Raman (Fig. 1). These lines (422, 529 cm^{-1}) are apparently due to vibrations involving predominantly Cu–ligand bond participation.

(*ii*). The redistribution of the intensity of the Raman lines in the spectrum of CuPE in comparison to that of Ph–C≡CH is noteworthy. The Raman spectrum of the latter compound exhibits characteristic lines, which may be attributed to the benzene ring, at about 1000, 1200 and 1600 cm^{-1}, and a very prominent line attribut-

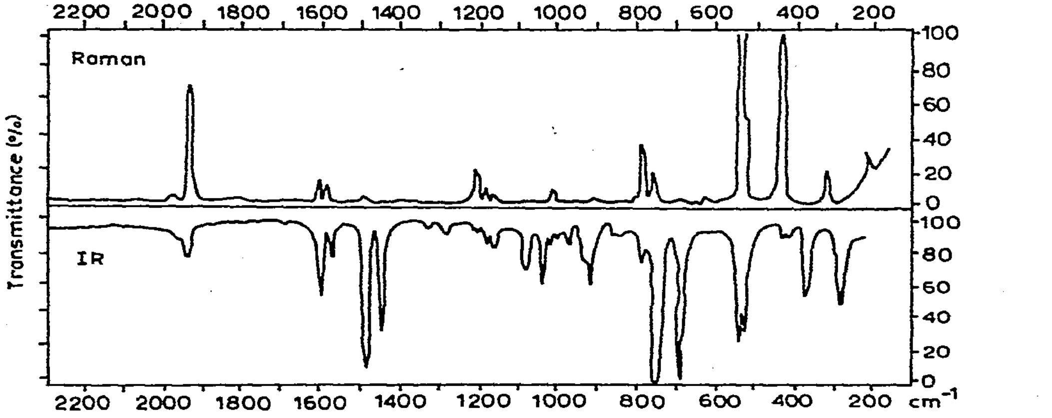

Fig. 1. The Raman and infrared absorption spectra of Ph–C≡C–Cu.

able to the C≡C bond. A considerable increase in the intensity of lines at 1200 and 1600 cm^{-1} by an order of magnitude in comparison with alkyl benzene compounds is a characteristic feature of (C≡C group)–(Ph-ring) conjugation. In the Raman spectrum of CuPE the lines at 1000, 1200 and 1600 cm^{-1} are relatively weak, but in addition to very strong lines in the spectral region 550–400 cm^{-1} an intense line at 780 cm^{-1} also appears, the latter having no natural counterpart in the spectrum of the "free" ligand. It may be pointed out that strong lines in this region have also been observed in the Raman spectra of other substituted copper(I) acetylides in which benzene rings have not been present. Thus this line appears in the spectra of alkylacetylides at ≈900 cm^{-1}. The considerable intensity of this line shows that in this mode, which appears to have a complicated form, the coordinates involving the coordination centre have a significant role. The nature of this line is now under investigation.

(*iii*). The assignment of a very strong Raman line at 1926 cm^{-1} in the spectrum of the complex to ν(C≡C) is unequivocal. However in comparison with PhC≡CH, a downward shift in the freqnency of this vibration of about 200 cm^{-1} is observed. In addition, a further line is also observed in this spectral region in the Raman spectrum, *i.e.* a weak line at 1971 cm^{-1}. Its origin may be attributed to two possible reasons, (*a*) this line may be due to a second-order transition enhanced by Fermi resonance with ν(C≡C) at 1926 cm^{-1}, or (*b*) both lines may belong to ν(C≡C) but of two different ligands whose C≡C bond lengths differ by an amount of 0.09 Å. The fact that the kinematic parameters of ν(C≡C) for substituted acetylenes are independent of the bond length has already been demonstrated[6]. However the above mentioned difference in the bond lengths could have significant influence on the dynamic parameters of ν(C≡C) (the force constants KC≡C), but this would in fact result in the observed downward shift of ν(C≡C) being far more than the observed value (45 cm^{-1}). In addition, the intensity of the line at 1971 cm^{-1} is rather small in comparison with that at 1926 cm^{-1} to allow the assignment of both these lines to vibrations associated with different C≡C ligands present in 1/1 ratio in the CuPE structure[4].

It is in fact known that the additional lines associated with ν(C≡C) in the Raman spectra of acetylenic compounds are quite specific to these compounds[7].

These data therefore suggest that the weak line which occurs in the spectrum at 1971 cm^{-1} is due to Fermi resonance and furthermore the spectral data provide no evidence for the presence of two different types of Ph–C≡C–ligands in the structure of CuPE as has been suggested elsewhere[4].

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