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INFRARED SPECTRUM AND VIBRATIONAL ASSIGNMENT OF π-ALLYLTRICARBONYLCOBALT

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SUMMARY

The infrared spectrum of π-allyltricarbonylcobalt has been recorded between 4000 and 300 cm^{-1}. The assignment of fundamental motions was essentially based on the crystal spectra in polarized light. The observed absorption pattern in the solid state seems to indicate that the molecule crystallizes in the monoclinic *Pm* or *Cm* space groups.

INTRODUCTION

In a previous paper we suggested a vibrational assignment for the complex π-allyl–$Fe(CO)_2NO$[1], based upon isotopic substitution within the allyl ligand and upon comparison with the spectra of π-allylhalogen and methyl-substituted complexes. It was shown that a valid criterion for the assignment of bands to their symmetry species could be given by the spectra of the oriented crystalline solid by means of polarized radiation.

This criterion is very useful in carrying out assignments for relatively intensely coloured, unstable complexes of this type for which reliable polarized Raman data are difficult to obtain.

The infrared spectrum of π-$C_3H_5Co(CO)_3$ is analysed in an attempt to extend our knowledge of the vibrational behaviour of transition metal π-allyl complexes. As in the iron complex, assignment of bands is based upon their polarization pattern in the solid state.

RESULTS AND DISCUSSION

A structure determination of π-allyltricarbonylcobalt recently investigated by means of electron diffraction reveals that the molecule possesses only a symmetry plane[2]. *A priori*, two approaches to the problem of deriving vibrational selection rules are possible. In the first, the molecule is considered as a whole and the overall symmetry C_s is used. If, on the other hand, the interactions between the organic and the inorganic fragments are low, it is more realistic to treat the complex in terms of the local symmetries of each fragment. In our case the local symmetry of the organic fragment is, without doubt, C_s[2,3] while that of the $-Co(CO)_3$ group is probably C_{3v}*. Only a detailed examination of spectroscopic results allows a choice to be made between these two approaches. We have found that on going from the liquid to the solid state, some bands, reliably attributed to the inorganic fragment, split into two components. Further, the magnitude of the separation in these components is such that the effect is definitely attributable to a lowering of the molecular symmetry in the crystalline site. Consequently, the free molecule must be treated using the local symmetry approximation when deriving selection rules. This is further confirmed by the fact that no combination bands involving vibrational levels of both fragments were found.

Table 1 lists the number and symmetry species of the normal modes for the organic and inorganic fragments. The IR crystal spectrum in polarized light, in the regions 2100–1900 cm^{-1} and 620–340 cm^{-1}, is shown in Fig. 1. Vibrational frequencies and assignments are collected in Table 2.

Since the orientation of crystal axes in the samples is unknown, the intensity of the fundamental at 1382 cm^{-1} has been chosen as a reference [as has that at 1387 cm^{-1} in π-allyl–$Fe(CO)_2NO$[1]].

In Table 2, "α" is the spectrum where this band has the lower intensity, and "β" the spectrum obtained upon 90° rotation of the polarizer with respect to the sample. Under these conditions comparison with the π-allyl–$Fe(CO)_2NO$ crystal spectrum[1] and Raman polarization data on π-allyl–$Mn(CO)_4$[4] shows that the "α" and "β" bands belong to A' and A'' symmetry species, respectively.

Vibrational assignment for the π-allyl–Co fragment

The vibrational absorptions of the allyl group in the complex fall at frequencies

TABLE 1

SYMMETRY OF THE NORMAL MODES FOR THE Allyl–Co AND $-Co(CO)_3$ FRAGMENTS[a]

π-Allyl–Co (*C_s symmetry*)		*$-Co(CO)_3$* (*C_{3v} symmetry*)	
ν(C–H)	A'		
$\nu(CH_2)$	$2A'+2A''$	ν(C–O)	A_1+E
$\delta(CH_2)$	$A'+A''$	ν(Co–C)	A_1+E
δ(C–H)	A''	δ(Co–C–O)	A_1+A_2+2E
π(C–H)	A'	δ(C–Co–C)	A_1+E
ν(C–C–C)	$A'+A''$	δ(allyl–Co–C)	E
$\rho_t(CH_2)$	$A'+A''$		
$\rho_w(CH_2)$	$A'+A''$		
$\rho_r(CH_2)$	$A'+A''$		
δ(C–C–C)	A'		
ν(Co–allyl)	$2A'+A''$		
τ(Co–allyl)	A''		

[a] All vibrations are IR active (except A_2 vibrations); ν, stretch; δ, deformation, π, deformation out of C–C–C plane, ρ_t, twist, ρ_r, rock; ρ_w, wag; τ, torsion

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* In fact, the (CO)–Co–(CO) angle perpendicular to the plane of symmetry is larger than the other two (CO)–Co–(CO) angles (109 and 100° respectively[2]), although differences of this order are usually spectroscopically undetectable

very similar to those found in the analogous iron complex. This fact clearly indicates that the electronic charge distribution and bonding situation of the organic fragment is influenced little, if at all, by the nature of the central metal and the ligands coordinated to it. This is yet further proof of the validity of the local symmetry concept for this kind of complex. Because of this, the same criteria for assignment as in ref. 1 are used, and Table 3 shows comparative data for the two complexes.

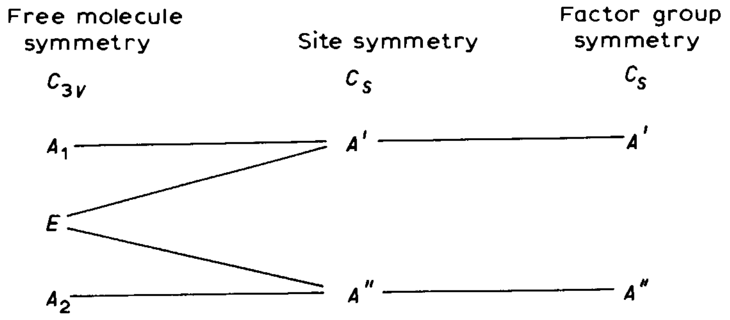
Vibrational assignment for the $-Co(CO)_3$ *fragment*

The vibrations of the $-Co(CO)_3$ group give rise to intense absorptions in the region 2100–1900 cm^{-1} and below 600 cm^{-1}. Attribution of bands to their symmetry species is based upon their different behaviour in the liquid and solid phase. In particular, the degenerate vibrations split into two components with opposite polarizations (α and β), while the totally symmetric vibrations give rise to single bands of type α in solid state spectra. The intense bands at 2062 and 1980 cm^{-1} (liquid phase) are then assigned to ν(C–O) (A_1 and E) stretchings, respectively. In the 600–300 cm^{-1} region, five intense absorptions may be unambiguously assigned to vibrations of the $-Co(CO)_3$ group, as predicted by the selection rules. On the basis of their behaviour in the crystal spectra, the bands at 590 and 458 cm^{-1} are assigned to A_1 species and those at 516, 482 and 366 cm^{-1} to E species. The attribution of these frequencies to the relative normal motions is not entirely conclusive due to the lack of an unequivocal criterion allowing a distinction to be made between Co–C stretchings and Co–C–O bendings, such as, for example, would be provided by isotopic substitution of oxygen and carbon. On the basis of existing literature data[5] we feel that bending vibrations can be assigned at higher frequencies than stretching vibrations (Table 2).

The band of β type found in the spectrum of the solid at 452 cm^{-1} and which has no corresponding band in the liquid, may be assigned to the pseudorotational bending mode Co–C–O of A_2 symmetry. The activation of such a mode in the solid state spectrum may be explained in terms of a lowering of molecular symmetry in the inorganic fragment, as discussed above.

Concluding remarks

The spectrum of π-allyl–$Co(CO)_3$ at liquid nitrogen temperature also provides useful information on the crystalline structure of this molecule. In fact, the splitting observed for the degenerate bands of the $-Co(CO)_3$ group may be interpreted only on the basis of the following correlation diagram:



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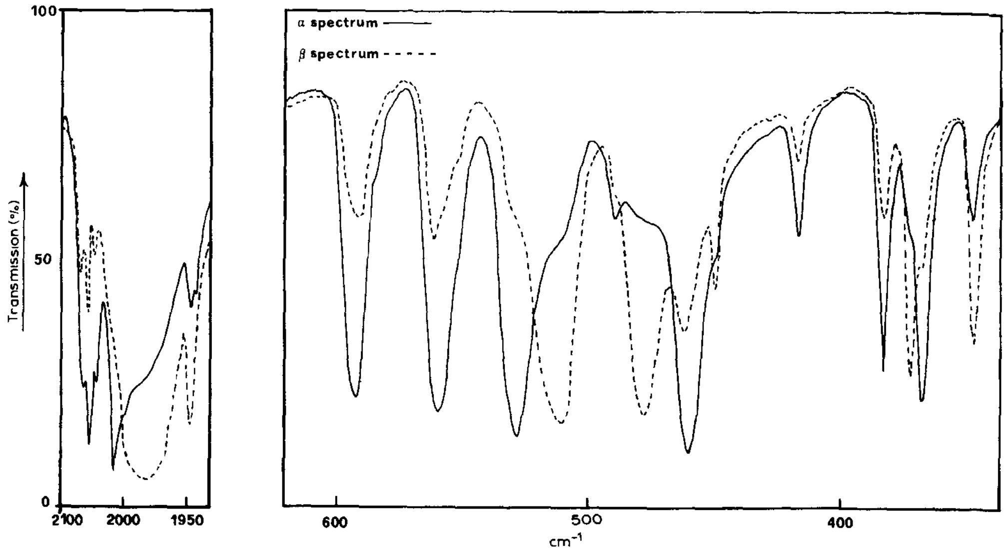

Fig 1 Infrared spectrum in the 2100–1900 and 600–300 cm^{-1} regions, of crystalline π-allyltricarbonylcobalt in polarized light at 100 K

TABLE 2

INFRARED SPECTRUM OF π-$C_3H_5Co(CO)_3$

Liquid	*Oriented crystal (T = 100 K)*	*Pol*	*Assignment*
3964 m			2 × 1980
3078 m	3090 m	β	$\nu(CH_2)A''$
3056 (sh)	3059 mw	α	$\nu(C\text{-}H)A'$
3014 m	3013 m	α	$\nu(CH_2)A'$
2955 w	2957 w		$\nu(CH_2)A''$
2930 w			2 × 1469
2922 w	2921 w	α	$\nu(CH_2)A'$
2854 vw			1469 + 1385
2763 vw			2 × 1385
2690 vw			1469 + 1224
2666 vw			1484 + 1186
2654 vw			1469 + 1186
2617 w			1385 + 1224
2574 w			2062 + 513
2542 w			2062 + 478
2480 w			2062 + 415
2460 m			1980 + 478
2401 vw			2062 + 340, 1469 + 932
2345 vw			1980 + 364
2245 w			1224 + 1017, 1469 + 772
2148 (sh)			1224 + 927
2062 vvs	2068 m 2056 ms 2045 m	α	$\nu(C\text{-}O)A_1$

(continued)

TABLE 2 (*continued*)

Liquid	*Oriented crystal* ($T = 100$ K)	*Pol*	*Assignment*
1980 vvs	2015 vs	α	$\nu(\mathrm{C{-}O})E$
	1978 vs	β	
	1946 m	β	$\nu(^{13}\mathrm{C{-}O})$
	1942 w	α	
1898 w			2 × 950, 1484 + 415
1875 w	1880 w	α	950 + 927
1864 w			2 × 932
1740 m			932 + 812, 1186 + 555
1702 vw			932 + 772
1641 vw			1224 + 415
1545 w			2 × 772
1484 s	1482 s	β	$\nu(\mathrm{C{-}C{-}C})A''$
1469 s	1468 s	α	$\delta(\mathrm{CH_2})A'$
1385 s	1382 ms	β	$\delta(\mathrm{CH_2})A''$
1324 w			772 + 555
1296 w			950 + 340, 735 + 555
1260 mw	1262 w(br)	$\alpha \simeq \beta$	927 + 340
1224 s	1229 ms	α	$\pi(\mathrm{C{-}H})A'$
1186 m	1182 ms	β	$\delta(\mathrm{C{-}H})A''$
1075 w(br)	1078 w(br)	$\alpha \simeq \beta$	735 + 340, 588 + 478
1017 s	1021 s	α	$\rho_t(\mathrm{CH_2})A'$
	1013 w	α	529 + 486
991 vw			513 + 478
950 ms	956 s	α	$\nu(\mathrm{C{-}C{-}C})A'$
932 s	938 s	β	$\rho_w(\mathrm{CH_2})A''$
927 (sh)	933 m	α	$\rho_w(\mathrm{CH_2})A'$
	925 m	β	561 + 370, 514 + 418
865 vw			525 + 340, 456 + 415
841 vw			478 + 364
812 mw	806 w	α	$\rho_r(\mathrm{CH_2})A'$
777 (sh)			456 + 364
772 s	795 ms	β	$\rho_t(\mathrm{CH_2})A''$
	761 w	α	2 × 382
735 vw	748 vw	β	$\rho_r(\mathrm{CH_2})A''$
588 vs	591 s	α	$\delta(\mathrm{Co{-}C{-}O})A_1$
555 vs	561 vs	α	$\delta(\mathrm{C{-}C{-}C})A'$
525 (sh)	529 s	α	$\delta(\mathrm{Co{-}C{-}O})E$
513 vs	514 s	β	
478 s	486 s	α	$\delta(\mathrm{Co{-}C{-}O})E$
	479 s	β	
456 s	461 vs	α	$\nu(\mathrm{Co{-}C})A_1$
	450 vw	β	$\delta(\mathrm{Co{-}C{-}O})A_2$
415 mw	418 mw	α	$\nu(\mathrm{Co{-}allyl})A'$
376 s	382 s	α	$\nu(\mathrm{Co{-}allyl})A'$
364 ms	371 s	β	$\nu(\mathrm{Co{-}C})E$
	366 s	α	
340 m	346 s	β	$\nu(\mathrm{Co{-}allyl})A''$

TABLE 3

ASSIGNMENTS OF π-allyl–Me VIBRATIONS IN π-$C_3H_5Fe(CO)_2NO$ AND π-$C_3H_5Co(CO)_3$ COMPLEXES

Assignments	*π-$C_3H_5Co(CO)_3$*	*π-$C_3H_5Fe(CO)_2NO$*
$\nu(CH_2)A''$	3078	3082
$\nu(C–H)A'$	3056	3048
$\nu(CH_2)A'$	3014	3016
$\nu(CH_2)A'$	2922	2968
$\nu(CH_2)A''$	2956	2932
$\nu(C–C–C)A''$	1484	1492
$\delta(CH_2)A'$	1469	1466
$\delta(CH_2)A''$	1385	1387
$\pi(C–H)A'$	1224	1229
$\delta(C–H)A''$	1186	1202
$\rho_t(CH_2)A'$	1017	1018
$\nu(C–C–C)A'$	950	966
$\rho_w(CH_2)A'$	927	926
$\rho_w(CH_2)A''$	932	916
$\rho_r(CH_2)A'$	812	778
$\rho_t(CH_2)A''$	772	752
$\rho_r(CH_2)A''$	735	722
$\delta(C–C–C)A'$	555	561
ν(Me–allyl)A'	415	417
ν(Me–allyl)A'	376	365
ν(Me–allyl)A''	340	335

Any other correlation would give rise to further splittings of a dynamic type (*i e* factor group splittings) for all the bands, which are not observed*. We suggest, from this data, that the complex crystallizes in the monoclinic system, as already found for the majority of transition metal carbonyl complexes investigated in the solid state[6].

Absence of information on the crystal density and the number of molecules in the unit cell, does not allow us to choose between the two monoclinic space groups, *Pm* (C_s^1) and *Cm* (C_s^3), which allow C_s symmetry for the site and the factor group.

EXPERIMENTAL

Materials

π-$C_3H_5Co(CO)_3$ was prepared as in the literature[3]. After repeated distillation *in vacuo* the complex was finally purified by gas chromatography[1].

Spectra

IR spectra between 4000 and 300 cm^{-1} were recorded on a P.E. model 521 grating spectrometer on both ligand and solid samples. Crystal spectra were obtained, using a conventional low-temperature cell, with polycrystalline oriented films at

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* It should be noted that the band assigned to the $\nu(C–O)$ vibration of A_1 symmetry shows a certain complexity in the solid state This is probably due to the strongly polar character of motions of this type which may lead to long distance intermolecular coupling such as to cause further splittings (see ref 7)

100 K. A P.E. grid polarizer unit was used for measurements with polarized radiation. Frequencies are accurate to ± 1 cm^{-1}.

We were unable to obtain reliable Raman data owing to the decomposition of the complex under our experimental conditions. However, when this manuscript was written, a paper by Andrews *et al.*[8] appeared reporting the laser Raman spectrum and assignment of this molecule. Our results are similar, although there are some discrepancies, especially with regard to the assignment of modes in the region below 700 cm^{-1}.

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