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The Vibrational Spectra of 2:2:1-Bicycloheptadiene and some of its Coordination Complexes

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Basing arguments principally upon Raman polarisation data partial assignments are given for the vibrational spectra of NBD, $Cr(CO)_4NBD$, $PdCl_2NBD$ and $PdBr_2NBD$ where NBD = 2,2,1-bicycloheptadiene. In particular the metal-olefin bond stretching modes are located ca. *250 cm^{-1}, the lowest known frequency for such vibrations, with the symmetric mode being the* higher *of the two. The positions of the coordination-lowered $\nu(C=C)$ frequencies are discussed.*

Introduction

Complex formation between an unsaturated hydrocarbon and a metal atom causes substantial changes in the vibrational spectrum of the ligand. For olefin complexes typified by Zeise's salt, $K[PtCl_3.C_2H_4].H_2O$, these shifts are now quite well understood, the principal features being a drop in $\nu(C=C)$ and a rise in the C-H out-of-plane deformation energies. As the complexity of the hydrocarbon ligand increases it becomes more difficult to make-cut assignments. This is particularly true of 2:2:1-bicycloheptadiene (norbornadiene), NBD, which forms a range of stable complexes with transition metals and has two vibrationally coupled (non-conjugated) C=C bonds. From a superficial study of the spectra of free and complexed NBD it is clear that a vibration *ca.* 1600 cm^{-1} is lowered some 150 cm^{-1} upon cordination but the detailed interpretation is far from simple as there seem to be too many bands in the region of interest.

We report a fairly complete vibrational study of $Cr(CO)_4NBD$, a particularly suitable compound for our purpose owing to its high solubility in several solvents, allowing study of the degree of polarisation of the Raman bands. In addition, less complete work on $PdX_2(NBD)$, (X = Cl, Br) is outlined.

Previous work[1-3] has been limited to recording lists of i.r. frequencies; no assignment other than to $\nu(C=C)$ being attempted. During the course of our study Baglin reported a detailed assignment of the ν(C-H) region of NBD itself.[4]

Results and Discussion

NBD. A recent electron diffraction study has confirmed the C_{2v} symmetry of this molecule.[5] Its normal modes of vibration are as follows, where the yz-plane passes through the methylene and bridgehead carbon atoms.

$$\Gamma(\nu\text{C-H}) = 3a_1 + a_2 + 2b_1 + 2b_2$$

$$\Gamma(\text{C-Hdef}) = 4a_1 + 4a_2 + 4b_1 + 4b_2$$

$$\Gamma(\text{skeletal}) = 5a_1 + 3a_2 + 3b_1 + 4b_2$$

We agree in most respects with Baglin's ν(C-H) assignment but reject his distinction between b_1 and b_2 modes as the experimental evidence on this point is too subtle to convince us. The principal feature of this region of the Raman spectrum is a surfeit of polarised bands; Baglin nicelyl accounts for the strongest bands on the basis of Fermi resonance with first overtones of i.r. bands at 1543 and 1453 cm^{-1}, but neglects weaker emissions. Our assignment is shown in Table I.

The essential features of this rather elaborate story are confirmed by the ν(C-H) spectra of the complexes. Considering $Cr(CO)_4NBD$ specifically, bands in the 1400-1600 cm^{-1} region are considerably affected by interaction with chromium thereby shifting first overtones away from positions suitable for Fermi resonance. ν(C-H) olefin drops back to its "undisturbed" position, 3085 cm^{-1}, and a pair of "undisturbed" $\nu(CH_2)$ vibrations is found at 2928 and 2961 cm^{-1}. Shifts in ν(C-H) olefinic upon cordination appear to be negligible but the bridgehead ν(C-H) rises by about 10 cm^{-1}.

In the region below 1650 cm^{-1} nine polarised bands are expected but eleven are found: this includes the bands at 424 and 1451 cm^{-1} which both have depolarisation ratios $\rho \sim .66$. Our ρ values for the other bands are close to the theoretical value 6/7. The region 1400-1700 cm^{-1} is expected to yield only *two* polarised bands, *viz*, $\nu(C=C)_s$ and $\delta(CH_2)$, whereas four are found. As with the ν(C-H) region, an explanation can be found in terms of overtones, see Table I. This region is further discussed below.

We have no evidence upon which to make an assignment of the lower frequencies of NBD but, on the basis of established correlations the labels given

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(1) E.W. Abel, M.A. Bennett, and G. Wilkinson, *J .Chem. Soc.*, 3178, (1959).

(2) R.A. Alexander, N.C. Baenziger, C. Carpenter, and J.R. Doyle, *J. Amer. Chem. Soc.*, *82*, 535 (1960).

(3) G.N. Schrauzer and S. Eichler, *Chem. Ber.*, *95*, 260 (1962).

(4) F.G. Baglin, *Spectroscopy Letters*, *3*, 149 (1970).

(5) T.W. Muecke and M.I. Davis, *Trans. Am. Cryst. Assoc.*, *2*, 173 (1966).

Table I. Vibrational frequencies/cm^{-1} of liquid 2:2:1-bicycloheptadiene.

Raman	I.r.	Assignment (C_{2v})
424s,P	420m	a_1, ν_{12} « butterfly » bend.
446s		a_2, ν_{20} ring torsion
506vvw	501m	
540vs	540w	
652vvw		a_2, ν_{17} $\delta(\geqslant$C-H)
730w,P	727vs,br	a_1, ν_{11} $\delta(\geqslant$C-H)
774vs,P	773vvw	a_1, ν_{10} π(C-H) olefinic
800w	798s	b_1 or b_2, π(C-H) olefinic
876vs,P	875s	a_1, ν_9 ν(C-C)
893s	893w	
914m	912w	
937vvs,P	935m	a_1, ν_8 ν(C-C)
949m		a_2, ν_{15} ν(C-C)
1018w	1017vw	
1065w	1062vvw	
1107vvs,P	1108vvw	a_1, ν_7 ν(C-C)
1153w	1152w	
1205w	1208m	
1225vs,P	1228m	a_1, ν_6 δ(C-H) olefinic
1240sh		a_2, ν_{14} $\rho_\tau CH_2$
1270wm	1270w	
~1319vw	1312s	
	1335sh	
	1390vvw	
1451m,P	1452m	a_1, ν_5 $\delta(CH_2)$
	1508vvw	
	1545s	b_1, ν_{23} ν(C=C)
1549w,P		A_1 2×774 = 1548
	1560vvw	
1575vs,P	1575vvw	a_1, ν_4 $\nu(C=C)_s$
1601m,P	1600vvw	A_1 2×798 = 1596
	1642w	
2867m,P	2870s	Fermi resonance of 2×1451 = 2902, A_1 with undisturbed
2932m,P	2935s	$\nu(CH_2)_s$ *ca.* 2900cm^{-1}.
2970w,br	2970sh	$\nu(CH_2)_a$,b_2; $\nu(\geqslant$C-H), b_1
2990s,P	2987s	$\nu(\geqslant$C-H) a_1
3048vvw,P		1601+1451 = 3053
3069w,br	3068s	ν(C-H) olefinic. b_1 or b_2
3064s,P		Fermi resonance of 2×1545 = 3090 with undisturbed
3102s,P	3100w	ν(C-H) olefinic *ca.* 3086cm^{-1}
3124w	3120w	ν(C-H) olefinic, b_2 or b_1
3145w,P	3140vvw	2×1575 = 3150

in Table I (especially to the polarised bands) are not unreasonable.

NBD Complexes. It is immediately clear from comparison of the spectra of NBD and the complexes that the polarised Raman bands at 1552, 1575 and 1601 cm^{-1} vanish upon coordination and are replaced by others in the 1390-1460 cm^{-1} region. From its frequency the 1451 cm^{-1} bands is most reasonably attributed to $\delta(CH_2)$. Only $\nu(C=C)_s$ is expected above this and is associated with the intense polarised band at 1575 cm^{-1}. Two possible origins for the 1601 cm^{-1} band are 2×798 or 727+875. The close mutual proximity of three totally symmetric modes *ca.* 1580 cm^{-1} suggests that there is little Fermi resonance between them which, in turn, indicates that the physical origin of the combining vibrations is not suitable for coupling to the $\nu(C=C)_s$ motion. Assignment of 798 cm^{-1} (i.r.) as π(olefinic), b_1 or b_2, would seem to meet this requirement. We assume that there is a small degree of resonance giving rise to some intensity sharing between 2×798 and $\nu(C=C)_s$; we postulate an industurbed position for the latter at 1580 cm^{-1}.

Consider the chromium complex: it shows polarised bands at 1429 and 1457 cm^{-1}. *A priori* we cannot tell whether these result from shifts of the 1451 and 1575 cm^{-1} NBD lines respectively or whether the correct correlation is 1451→1457, 1575→1426 cm^{-1}. We prefer the latter as there is a constant feature in all of the spectra of the complexes and of the ligand close to 1455 cm^{-1}; we attribute this to $\delta(CH_2)$ of the bridgehead methylene group, which would be unaffected by complex formation. This leaves $\nu(C=C)$ in the chromium complex 146 cm^{-1} or 9.3% lower than the value in free NBD, a value comparable with those found for mono-olefin complexes.[6]

In the same region the palladium compounds show much richer spectra, although some of the complexity is probably due to correlation coupling in the solid. There should, of course, be *two* lowered $\nu(C=C)$ frequencies but only one was apparent in the chromium complex. For the palladium cases we associate the 1408 and 1443 cm^{-1} bands (chloride) and their analogues in the bromide with these two vibrations.

There is an ambiuguity in the assignment of the $\nu(C=C)_a$ mode in the free ligand. The weak 1642 cm^{-1} band is in the normal range for a double bond

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(6) D.B. Powell and T.J. Leedham, *Spectrochim. Acta.*, *28A*, 337 (1972).

stretch. On the other hand the C=C bond in NBD is rather longer than usual, 1.52 Å, suggesting that it is more logical to take the stronger 1545 cm^{-1} i.r. bands as $\nu(C=C)_a$. In this case we represent the frequency changes upon coordination by the correlation:

NBD	1575	1545
$PdCl_2NBD$	1443	1408
Lowering	132	139 cm^{-1}
	8.4	9.0 %

Several of the NBD bands below 1300 cm^{-1} can be clearly identified in the spectra of the complexes, notably the strong polarised features at 876, 937, 1107 and 1225 cm^{-1} which occur throughout the series with realtively minor shifts. The 774 cm^{-1} band can also be identified, though with less confidence. Thc difficulty comes in the region below 700 cm^{-1} in which the spectra of these compounds are complex and cannot be assigned in detail without much more information. Nevertheless, on the available evidence it is possible to understand the most chemically significant parts of the spectra, those associated with the coordinated olefin.

Cordination of NBD to hypothetical $PdCl_2$ adds the following modes to the ligand spectrum.

a_1	ν(Pd-ol.)$_s$	b_1	ν(Pd-ol.)$_a$
	ν(Pd-X)$_s$		ν(Pd-X)$_a$
	$\delta(PdX_2)_s$		PdX_2rock/δ(X-Pd-ol.)
a_2	Torsion/PdX_2twist	b_2	(Pd-ol.)tilt(1)
			PdX_2wag/π(X-Pd-ol.)

where ol. ≡ NBD. The tilt(1) mode corresponds roughly to a rotation about the C_{2v} x-axis passing through the C=C centres, see Figure 1. Ring tilt modes in (π-C_5H_5) and π-arene complexes come at higher frequency than corersponding M-ring bond stretching vibrations and there is no reason to expect the order to be different in NBD complexes. There will be another mode which also has some of the nature of a "tilt"; it corresponds to the a_2 torsion of the free ligand framework which can only be executed in a complex with accompanying stretching of M-ol. bonds, see Figure 1.

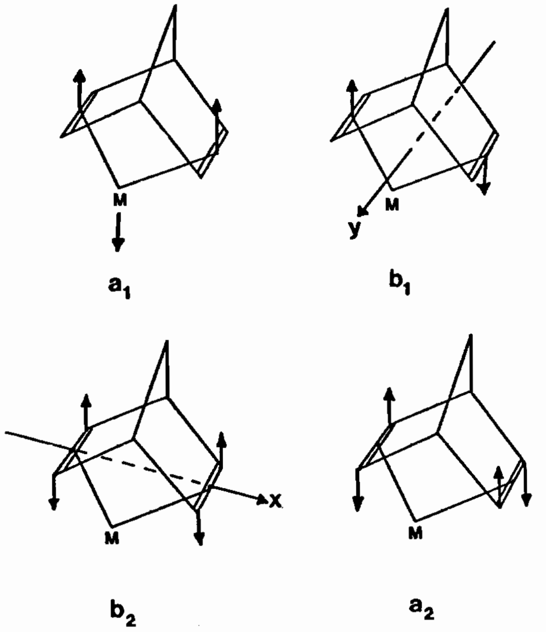

Figure 1. Skeletal modes of coordinated NBD. ν(M-ol.)$_s$ (a_1), ν(M-ol.)$_{as}$ (b_1) tilt (1) (b_2), and olefin torsion/tilt (2) (a_2).

Carbonyl complexes show ν(M-CO) and δ(MCO) modes in the region 350-650 cm^{-1} with δ(CMC) below 150 cm^{-1} but are invariably clear between these regions. The Raman lines of $Cr(CO)_4NBD$ at 249 (P) and 237 cm^{-1}, together with their i.r. equivalents, can therefore be assigned to ν(Cr-ol.)$_s$ and ν(Cr-ol.)$_{as}$(b_1) the order being that required by the solution polarisation results. These are the lowest reported M-olefin stretching frequencies, though their values can be predicted approximately on the assumption that ν(M-ol.) is determined principally by the mass of the olefin. Thus, taking ν(Pt-C) in Zeise's salt at 452 cm^{-1} (average of the two Pt-C stretches) and substituting the mass of NBD, ν(Pt-NBD) is estimated at 250 cm^{-1}. For $PdCl_2NBD$ the observed frequencies/cm^{-1} are 265, 233 with a rise to 304, 254 for $Fe(CO)_3NBD$ (for which we have obtained preliminary data only) probably reflecting the lighter mass of the metal rather than increased M-C bond strength.

Because the tilt(1) mode is expected above ν(M-ol.) we seek evidence for it in the PdX_2NBD spectra rather than in those of the carbonyl compounds which are complicated in the region of interest by ν(M-CO) and δ(MCO) modes. νPd-Cl) is at 304(b_1), 338(a_1) cm^{-1} in $PdCl_2NBD$ with both bands showing signs of isotopic fine structure. In $PdBr_2NBD$ ν(Pd-Br) now overlays the intense ν(Pd-ol.) bands *ca.* 250 cm^{-1} but has revealed a band at 305 cm^{-1}, presumably present in the chloride, though overlaid by ν(Pd-Cl)$_s$, a_1 which is rather broad. As no ligand mode occurs in this region we tentatively label this band as tilt(1), b_2, a suggestion strengthened by the fact that it is very close to the ν(Pd-Cl) modes at 308, a_1 and 337, b_1 thereby indicating that its symmetry differs from theirs.

We have yet to locate the NBD torsion/tilt(2) mode. Since this is a modified NBD vibration of a_2 symmetry it must be associated with a band present only in the Raman spectrum. The band at 446 cm^{-1} in the NBD spectrum meets this requirement; we tentatively associate it in the complexes with 487 cm^{-1} (chloride), 483 cm^{-1} (bromide). Apart from this band, all others above 350 cm^{-1} for the PdX_2NBD complexes must originate in the ligand spectrum. Between 350 and 600 cm^{-1} we find in the Raman spectrum of the chloride: 487, 518P, 593 cm^{-1}. (Only the 518 cm^{-1} band was found in solution due to low solubility). Similar frequencies are exhibited by the bromide. Comparison with free NBD shows that since the 424 cm^{-1} band is the only polarised one in this region it must have shifted up to 518 cm^{-1} upon coordination, consistent with its assignment as the a_1 "butterfly" skeletal deformation. In support of this proposal we note that the C_2-C_1-C_6 angle is reduced from 106.6°[5] to 98.3°[7] upon coordination.

Below 200 cm^{-1} we expect four internal modes

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(7) N.C. Baenziger, J.R. Doyle, and C. Carpenter, *Acta Cryst.*, *14*, 303 (1961).

Table II. Vibrational frequencies/cm^{-1} and assignment for PdX_2NBD.

X = Cl			X = Br	
Raman	I.r. (ambient)	Assignment	Raman	I.r.
67m			49w	
82w	92w		71vvw	
	106w			
117w	116w		119w	
129s		a_2		
145vs	147w	a_1, $\delta(PdX_2)$	93s	
167w			169wm	
181w	178w		185wm	
233w	238s	b_1, ν(Pd-ol.)$_a$	205vs [a]	
265vs	268vs	a_1, ν(Pd-ol.)$_s$	229s	
305m,br	304vs	b_2, Tilt(1)+a_1, ν(Pd-Cl)$_s$	305m	
337w	338vs	b_1, ν(PdCl)$_a$		
	382m			
487wm	491wm	a_2, NBD torsion/Tilt(2)	483w	486vvw
518vs, P [b]	516vs	a_1, ν_{12} «butterfly» bend	515s	508vvw
595m	589vvw		589m	591vvw
	687vw			
772vvw	770vs			769s
	791vs		791vvw	781s
801vvw	798s			
	807w			806m
	822sh			812m
825vvw	827ms			
883w	880m	ν_9		
898w	896sh		893m	893m
	899ms			931vw
945w	940s	ν_8	943wm	937w
953vw	956vvw			
	967s			957s
			972vvw	
	1007vvw			996vvw
				1033w
	1048vw			1038w
1085s	1085m	ν_7	1083vs	1080w
	1105vvw			
1125wm			1127w	
1163vvw	1158ms		1162vvw	
1177vvw	1176ms		1181vvw	1175s
	1185s			
1227wm	1227s	ν_6	1223wm	1225m
	1258vw			1242m
	1305sh			
	1310vs			1310s
	1395wm			1375m
1406wm	1408vs		1408m	1410wm
1422vw	1422wm	ν(C=C)		1420m
1431w				
1443w	1443wm		1445m	1440m
1453vvw	1452wm	ν_5, $\delta(CH_2)$		
2898vvw	2895w			
2922wm	2920wm			
2943vvw				
2965wm	2965wm			
3037s	3040sh			
	3048s			
3058wm	3059s			
3089w	3088w			
3101wm	3100w			

[a] Due to ν(Pd-ol.) and ν(Pd-Br) but cannot be assigned individually. [b] In CH_2Cl_2 solution.

loosely described as $\delta(PdX_2)$, and PdX_2 rock, wag and twist, together with many lattice modes. From its chloride-bromide shift $\delta(PdCl_2)$ is is reasonably placed at 145 cm^{-1} (93 cm^{-1} in the bromide), but we have no evidence upon which to base further assignments. However, it is quite clear from the *numbers* of bands in the 150 to 350 cm^{-1} regions of these two complexes that we are correct in placing at least some of the M-olefin skeletal modes in this region, because there are too many bands to be accounted for otherwise.

Having reached some understanding of the PdX_2-NBD spectra we can outline further assignments for the more complicated vibrational pattern of the carbonyl complex, see Table III. Polarised bands at 411 and 456 cm^{-1} are principally ν(Cr-CO) modes, (two a_1 Cr-C stretches are expected) and the "butterfly" bend is at 499 cm^{-1}. The weak 553 cm^{-1} band is probably polarised and, if so, is one of the two predicted δ(Cr-CO) modes: such vibrations nearly always generate

Table III. Vibrational frequencies/cm^{-1} and assignments for $Cr(CO)_4NBD$.

Raman Solid (ambient temp.)	Raman Solid (liquid N_2 temp.)	Raman Solution	Ir. Solid (ambient temp.)	Ir. Solid (liquid N_2 temp.)	Ir. Solution	Assignment
55w	57w			54w		
85w	88w					
				98m		
110vs	112vs		114m			
122vs	126vs			128sh		
145w	150s		144sh	146vvw		
165w			168sh			
183w			180w			
234sh						
243m	246m	237wdP	242s	244vs		b_1, ν(Cr-ol.)$_a$
255s	255m	249sP	257sh	257s		a_1, ν(Cr-ol.)$_s$
			282w	296sh		b_2, Tilt (1)
413vs	418vs	411vsP			403	
				452	448w	a_1, ν(Cr-CO)$_s$
458vvs	462vs	456sP	451	456		
				466sh	467	
461sh	474wm	470w	466m	469m		
463m						
	504m	499wmP	489w	484w	495	a_1 « butterfly » bend
499m			498vvw	492w		
539w	524w		511m	512sh	515m	
	544vw			516m		
556w	558w	553vw?P	539w	540sh		a_1, δ(CrCO)
				542wm		
609w	612w	599vvw	603m	605m	602s	
624wm	628wm		634m	640m	638s	
675wm	678wm	675wP	670s	665m	669s	
755wm	758w		751w	752w	760wm	
773w	776w		770m	772wm		
			787w	787w	787w	
			803w	806w	798vvw	
			868w	868wbr		
886w	888w	885w	885w	885w		a_1, ν_9
			901w	901w	901w	
			919w	919w		
931m	932m	931sP	934w	935w	929w	a_1, ν_8
	939sh					
953w	950w	950vw	947w		946w	a_2
			1005w	1005vvw		
1044w	1044w	1045w			1043vvw	
1089m	1092wm	1090sP	1087wm	1090m	1090vvw	a_1, ν_7
1111w	1116w	1110mw	1109mw	1112w		
			1162mw	1165w	1160vvw	
1185w	1184w	1185w	1180m	1180wm	1183w	
1229m	1230m	1227mP	1238			a_1, ν_6
			1258vvw	1258w		
			1305m	1308wm	1312w	
1426wm	1428m	1429w	1430w	1432sh	1430w	ν(C=C)
	1433sh					
1458m	1460m	1457mP	1453vvw	1460s (br)	1458m	a_1, ν_5 δCH_2
1880vs	1879s		1865br,s			
1903vw	1902vw	1903w			1903s	b_2 ν(CO)^a
1921w	1924w			1925m		
1939vvs	1945s	1953w	1930br,s		1935s	a_1
1960w	1963w				1952s	b_1
2020m	2024m	2029sP	2025vs	2028s,br	2028s	a_1
			2845m		2845w	ν(C-H)
2935wbr			2930s		2923w	
2965wbr			2962w		2960m	
3000m			3000s		3000m	
3011wm			3010s			
3080wm			3080w		3080vw	
3098wm			3095mw		3090vw	

[a] Assignment applies to solution values only.

very weak Raman bands. In the ν(CO) region a classic C_{2v} tetracarbonyl pattern is exhibited in the solution spectra. The depolarisation ratio of the lower a_1 mode is close to 6/7 and therefore does not assist the assignment, but use of the Cotton-Kraihanzel equations[8] yields the assignment of Table III. The more complex solid state Raman spectrum cannot be understood in detail until we have determined the unit cell

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(8) F.A. Cotton and C.S. Kraihanzel, *J. Amer. Chem. Soc.*, *84*, 4432 (1962).

symemtry and occupancy, but is probably generated by a bimolecular cell.

Discussion

The major point of interest arising from this study is location of the M-olefin stretching modes *ca.* 250 cm^{-1} with the *higher* of the two being the totally symmetric one. Simultaneous removal of both olefinic double bonds is an unfavourable process with respect to the antisymmetric mode (in which one is removed whilst the other moves closer in) because the latter allows strengthening of one M-olefin bond as the other is weakened whilst the former does not. This is analogous to the metal carbonyl situation in which totally symmetric ν(CO) modes are at higher frequency than antiphase modes.[9]

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(9) L.E. Orgel, *Inorg. Chem.*, *1*, 25 (1962).