Vibrational Spectra of Cyclopentadienylnickel Nitrosyl and its Pentadeuterio- and ^{15}NO Derivatives

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The i.r. and Raman spectra of C_5H_5NiNO have been studied and, with the aid of C_5D_5NiNO and $C_5H_5Ni^{15}NO$ isotopes, it has been possible to reassign some fundamentals.

BECAUSE of its high symmetry and well defined structure,[1] cyclopentadienylnickel nitrosyl may be regarded as a model molecule for spectroscopic studies of monocyclopentadienyl π-complexes with transitional metals. Although the vibrational spectrum has already been investigated,[2,3] the assignments suggested for some fundamentals can be considered rather uncertain owing to the lack of data on isotopic analogues. The present study was undertaken to check earlier assignments and to get a reliable vibrational analysis for the parent molecule, with the aid of H–D and ^{14}N–^{15}N isotopic shifts.

EXPERIMENTAL

Materials.—C_5H_5NiNO was purchased from Strem Chemicals Inc. and purified by g.l.c. $C_5H_5Ni^{15}NO$ was prepared from nickelocene and 98% ^{15}NO in n-pentane[4] and purified by g.l.c. C_5D_5NiNO was prepared in the same way, starting from [$^2H_{10}$]nickelocene which was synthetized from $NiBr_2$ and C_5D_6 with triethylamine as catalyst instead of diethylamine[5] (which exchanges with C_5D_6). For the synthesis of [$^2H_6$]cyclopentadiene the method suggested by Gallinella[6] was followed. In a typical run, to hexamethylphosphorotriamide (250 ml) were added, in order and in a dry-box, freshly distilled C_5H_6 (30 ml), 99·75% D_2O (60 ml), and 40% NaOD solution (1·85 ml). After 2 h the brown mixture was quickly distilled at atmospheric pressure with a high-efficiency fractionating column. The i.r. spectrum of the product (C_5D_6), collected at -80 °C and dried (Na_2SO_4), showed *ca.* 50% of deuterium. Two other exchanges performed in the same way gave a final product with 98% of deuterium (i.r. check).

Spectra.—I.r. spectra, in the 4000—250 cm^{-1} region, were recorded with a Perkin-Elmer Model 521 grating spectrometer, calibrated with water vapour and indene peaks. The frequencies of sharp bands are accurate to ± 1 cm^{-1}. KBr and CsI sealed microcells, with 0·025 and 0·1 mm thicknesses, were used for the spectra of liquids. Vapour-phase spectra were measured, at various pressures, in 10 cm glass cells with CsI windows. Far-i.r. spectra were recorded with a Beckman IR 11 spectrometer, in polyethylene moulded cells.

The laser Raman spectrum of liquid C_5H_5NiNO was recorded with a Jarrell-Ash spectrometer; the source was a 60 mW He–Ne lamp (6328 Å). A double-pass 20 μl cell was used with 90° scattering.

Spectra are shown in the Figure and frequencies listed in Tables 1—3. Assignments of the fundamental modes of the three isotopic species are collected in Table 4.

RESULTS AND DISCUSSION

C_5H_5NiNO has C_{5v} molecular symmetry[1,7] and its 33 fundamental motions can be classified as follows according to the symmetry and activity: $6A_1$ (i.r., Raman polarized); $1A_2$ (inactive); $7E_1$ (i.r., Raman depolarized); $6E_2$ (Raman depolarized).

Vibrational Assignments.—*A_1 vibrations.* The Raman polarization data and the ratios of frequency shift (H : D), substantiate the previous assignments for vibrations of

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[1] A. Peter Cox and Alan B. Brittain, *Trans. Faraday Soc.*, 1970, **66**, 557.

[2] R. D. Feltham and W. G. Fateley, *Spectrochim. Acta*, 1964, **20**, 1081.

[3] I. J. Hyams and E. R. Lippincott, *Nature*, 1967, **214**, 267.

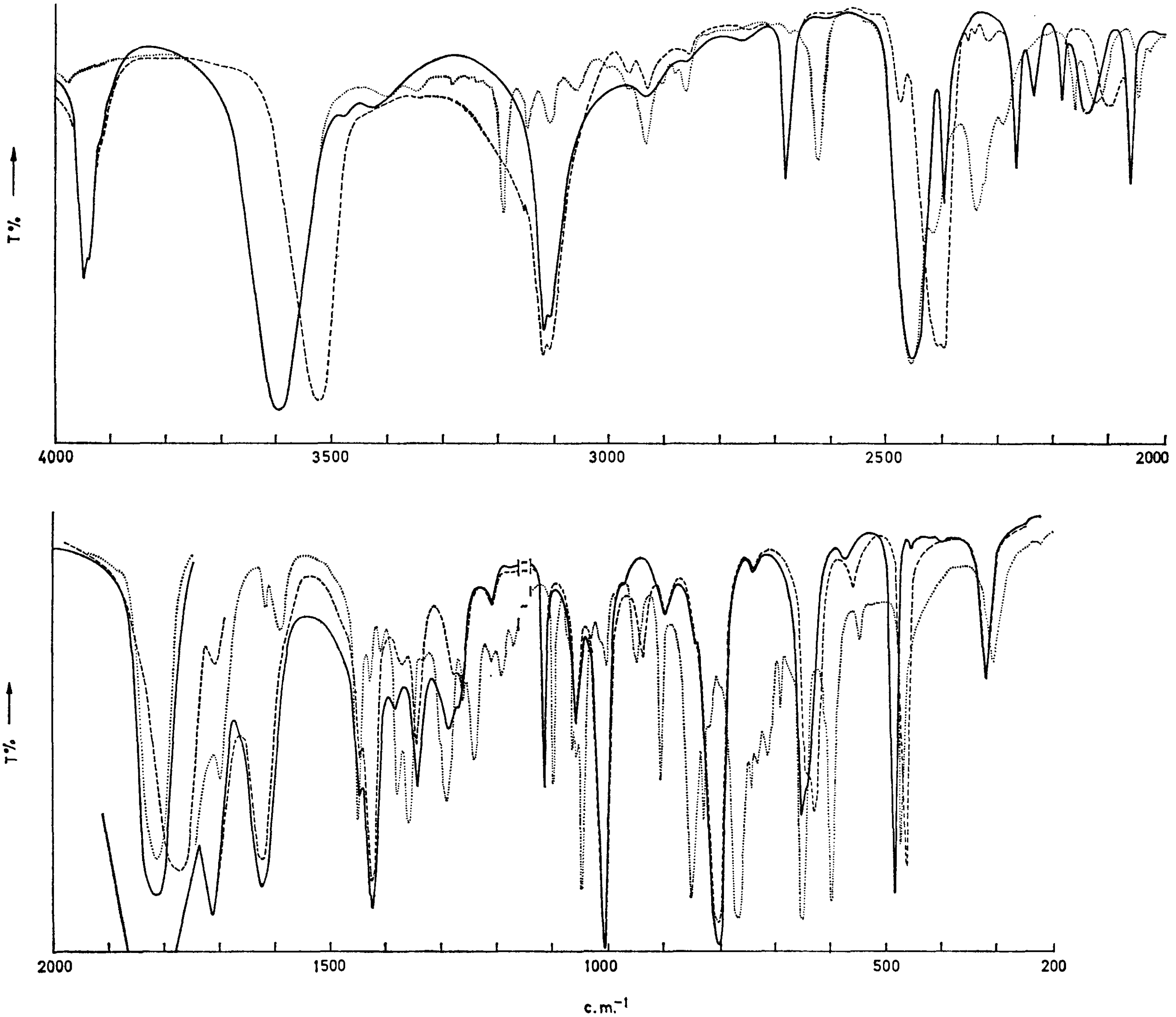
[4] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

[5] J. J. Eisch and R. B. King, *Organometallic Synth.*, 1965, **1**, 169.

[6] E. Gallinella, personal communication.

[7] A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, 1958, **181**, 1157.

this symmetry species.[2,3] In the vapour spectrum of C_5H_5NiNO there is a weak band at 1112 cm^{-1} with rotational structure and *ca.* 10 cm^{-1} *R–P* separation. Such a separation is that predicted for a parallel motion by the Seth-Paul method.[8] Consequently the vapour-phase band cannot be assigned, as in the liquid, to the perpendicular breathing mode, and we believe it may be the $\nu_4 + \nu_6$ combination (parallel mode).



Infrared spectra of liquid C_5H_5NiNO ——; C_5D_5NiNO • • • •; $C_5H_5Ni^{15}NO$ - - - -

In the spectra of both H_5 and D_5 complexes an absorption at 649 cm^{-1} is found. In the ^{15}NO spectrum this band shifts to 642 cm^{-1} and another peak is observed at 634 cm^{-1}. We correlate the 649 peak with that at 642 cm^{-1} in the ^{15}NO molecule and attribute these bands to the Ni–N stretching motion. The isotopic shift is 7 cm^{-1}, compared with a value of 5 cm^{-1} predicted for such a mode.[9] The peak at 634 cm^{-1} in ^{15}NO species should correspond to the first overtone of the ring–Ni stretching mode (near 320 cm^{-1}), which is located at 640 cm^{-1} in the light compound. Since in the ^{15}NO molecule it falls nearer to the Ni–N stretching mode, it produces stronger Fermi coupling with this fundamental; therefore it appears at lower frequency and with enhanced intensity than in the light compound.

The Teller–Redlich product-rule for A_1 vibrations gives a ratio of 0·496 compared with a theoretical one of 0·508.

E_1 vibrations. The peak at 3105 (H_5 and ^{15}NO species) is attributed to the degenerate C–H stretching of E_1 symmetry; in the D_5 molecule it corresponds to the band at 2286 cm^{-1} (H : D ratio = 1·36).

[8] W. A. Seth-Paul, *J. Mol. Structure*, 1969, **3**, 409.

[9] (*a*) G. Paliani, A. Poletti, and A. Santucci, *J. Mol. Structure*, 1971, **8**, 63; A. Poletti, A. Santucci, and G. Paliani, *Spectrochim. Acta*, 1971, **27**, *A*, 2061; (*b*) Eiichi Miki, *Bull. Chem. Soc. Japan*, 1968, **41**, 1835.

At 1425 cm^{-1} (1424 in $C_5H_5Ni^{15}NO$) is found, in the liquid spectrum, a rather intense band which shifts, upon deuteriation, to 1296 cm^{-1} (H : D ratio = 1·10). In the vapour this band has a gaussian profile as required for a perpendicular motion; therefore it is assigned as the degenerate C–C stretching, in contrast with the assignment of Hyams and Lippincott.[3]

TABLE 1

I.r. and Raman spectra of C_5H_5NiNO

I.r. vapour	Liquid		Assignment
	I.r.	Raman	
3944w	3942m		$\nu_8 + \nu_{19}$
	3936sh		$\nu_{15} + \nu_{19}$
3648m	3592s		$2\nu_2$
3118m	3115s	3120w (p)	ν_1
	3105sh		ν_8
		3098w (dp)	ν_{15}
	2919vw		$\nu_2 + \nu_3$
2680w	2677m		$2\nu_{16}$
2483m	2450s		$\nu_2 + \nu_5$
2393w	2391m		$\nu_{10} + \nu_{16}$
2264w	2262m		$\nu_9 + \nu_{19}$
2233w	2232w		$\nu_4 + \nu_9$
	2181w		$\nu_{16} + \nu_{19}$
2155w	2130mw,br		$\nu_2 + \nu_6$
2063w	2057m		$\nu_{10} + \nu_{11}$
1836vs	1809vvs	1803w (p?)	ν_2
1697m	1705m		$\nu_5 + \nu_{10}$
1610m	1621s		$\nu_{10} + \nu_{20}$
1438sh	1445sh		$\nu_4 + \nu_5$
1422m	1425s		ν_9
	1379w		$\nu_6 + \nu_{10}$
1340vw	1343mw	1343vw (dp)	$\nu_{10} + \nu_{13}$; ν_{16}
1288vw	1285w		$\nu_4 + \nu_{12}$
1260vw	1261vw		$\nu_{13} + \nu_{18}$
	1207vw		$\nu_3 + \nu_{14}$
R 1117			
Q 1112m	1112s	1114s (p)	ν_3
P 1107			
1053w	1054s	1056w (dp)	ν_{10}
1005vs	1005vs	1007w (dp)	ν_{11}
	970sh	964mw (dp)	$2\nu_{12}$; ν_{18}
R 888			
Q 885w	893m		$\nu_4 + \nu_{14}$
P 878			
	841sh	840vw	$\nu_{13} + \nu_{20}$; ν_{19}
R 808			
Q 803vs	799vs	806w (p?)	ν_4
P 798			
	738w		$2\nu_{14} + \nu_{20}$
649s	649s	650m (p)	ν_5
640sh	640sh	633sh	$2\nu_6$
562w,br	569w	565w	$\nu_{12} + \nu_{14}$; ν_{20}
485s	s484s	486vw	ν_{12}
315m	322m	322s (p)	ν_6
	290sh		ν_{13}
	188w,br		$2\nu_{14}$
		92s	ν_{14}

s = Strong; m = medium, w = weak, br = broad, v = very, (p) = polarized; (dp) = depolarized.

The band at 1005 cm^{-1} (Raman 1007dp) is assigned as previously reported,[2] essentially for its gaussian contour and the isotopic shift. The corresponding parallel C–H bend of E_1 symmetry absorbs at 1054 cm^{-1} (Raman 1056dp) and shifts at 852 cm^{-1} in the D_5 molecule (H : D ratio = 1·24).

The absorption at 484 cm^{-1} (478 in the D_5 molecule) is easily assigned to the Ni–N–O bending mode because in the ^{15}NO molecule it shifts to 470 cm^{-1}.

The ring-tilt mode was assigned by Hyams and Lippincott[3] to the Raman line at 252 cm^{-1}. We have not found any absorption in this region, neither in the far-i.r. nor in the Raman spectrum. However in the i.r. spectrum we observed an absorption at 290 cm^{-1} in both H_5- and ^{15}NO-molecules. Since for methylcyclopentadienylnickel nitrosyl the same tilting mode has been assigned[10] at 298 cm^{-1} we suggest that the present absorption at 290 cm^{-1} should be attributed to the tilt vibration.

TABLE 2

I.r. spectrum of C_5D_5NiNO

Liquid	Assignment	Liquid	Assignment
3592s	$2\nu_2$	1296m	ν_9
3184mw	$\nu_1 + \nu_{10}$	1267vw	$\nu_{18} + \nu_{20}$
3140w	$\nu_8 + \nu_{10}$	1247mw	$\nu_4 + \nu_5$
3098w	$\nu_2 + \nu_9$	1217vw	$\nu_{12} + \nu_{18}$
3048vw	$\nu_8 + \nu_{11}$	1198vw	$\nu_2 - \nu_4$
2926w	$\nu_1 + \nu_4$	1176vw	$\nu_2 - \nu_5$
2852vw	$\nu_2 + \nu_3$	1103m	$\nu_9 - 2\nu_{14}$
2612mw	$\nu_6 + \nu_8$	1066m	$\nu_4 + \nu_{12}$
2451ms	$\nu_2 + \nu_5$	1052s	ν_3
2416sh	$2\nu_{16}$, $\nu_2 + \nu_4$	1010vw	$\nu_{12} + \nu_{20}$
2335mw	ν_1	956w	$2\nu_{12}$
2286vw	ν_8	910m	$\nu_4 + \nu_6$
2160w	$\nu_9 + \nu_{11} + \nu_{14}$	852s	ν_{10}
2120w,br	$\nu_3 + \nu_4 + \nu_{12}$	832mw	$\nu_{14} + \nu_{18}$
2042w	$\nu_9 + \nu_{18}$	771s	ν_{11}
1952sh	$\nu_{16} + \nu_{18}$	749w	$\nu_2 - \nu_3$
1808vvs	ν_2	737vw	$\nu_5 + \nu_{14}$
1703w	$\nu_3 + \nu_6$	716vw	$2\nu_{14} + \nu_{20}$
1623vw	$\nu_{10} + \nu_{11}$	689mw	$\nu_4 + \nu_{14}$
1594w	$\nu_9 + \nu_6$	649vs	ν_5
1455m	$\nu_4 + \nu_{10}$	600vs	ν_4
1434vw	$\nu_3 + \nu_6 + \nu_{14}$	551w	$2\nu_{13}$
1413vw	$\nu_5 + \nu_{11}$	534vw	ν_{20}
1383mw	$\nu_{10} + \nu_{20}$	478vs	ν_{12}
1363m	$\nu_4 + \nu_{11}$	298ms	ν_6

TABLE 3

I.r. spectrum of $C_5H_5Ni^{15}NO$

Liquid	Assignment	Liquid	Assignment
3942m	$\nu_8 + \nu_{19}$	1443sh	$\nu_4 + \nu_5$
3936sh	$\nu_{15} + \nu_{19}$	1424s	ν_9
3518s	$2\nu_2$	1368vw	$\nu_6 + \nu_{10}$
3115s	ν_1	1341mw	$\nu_{10} + \nu_{13}$
3105sh	ν_8	1268sh	$\nu_4 + \nu_{12}$
2959vw	$\nu_2 + \nu_3 + \nu_{14}$	1261w	$\nu_{13} + \nu_{18}$
2927vw	$\nu_2 + \nu_{10} + \nu_{14}$	1205vw	$\nu_3 + \nu_{14}$
2852vw	$\nu_2 + \nu_4 + \nu_{13}$	1111s	ν_3
2677m	$2\nu_{16}$	1054s	ν_{10}
2469w	$\nu_1 - \nu_5$	1005vs	ν_{11}
2402s	$\nu_2 + \nu_5$	939w	$2\nu_{12}$
2391sh	$\nu_{10} + \nu_{16}$	894mw	$\nu_4 + \nu_{14}$
2262m	$\nu_9 + \nu_{19}$	799vs	ν_4
2232w	$\nu_4 + \nu_9$	738w	$\nu_{20} + 2\nu_{14}$
2181w	$\nu_{16} + \nu_{19}$	642sh	ν_5
2098w,br	$\nu_2 + \nu_6$	634ms	$2\nu_6$
2057m	$\nu_{10} + \nu_{11}$	555w	$\nu_{12} + \nu_{14}$
1774vvs	ν_2	470s	ν_{12}
1706mw	$\nu_9 + \nu_{13}$	321ms	ν_6
1619ms	$\nu_{10} + \nu_{20}$	290sh	ν_{13}

We are also not in agreement with Hyams and Lippincott[3] for the assignment of the last E_1 vibration, the ring–Ni–N bend, since we have not found lines around 150 cm^{-1} in the Raman spectrum. However in the far-i.r. spectrum there is a weak-broad absorption at 188

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[10] R. T. Bailey, *Spectrochim. Acta*, 1969, **25**, *A*, 1127.

cm^{-1} and in the Raman spectrum a strong line at 92 cm^{-1}. We assign the Raman line to the ring–Ni–N bending mode, and the i.r. band to its first overtone. Unfortunately we are unable to observe the last two frequencies experimentally in the D$_5$-molecule. Therefore only an approximate product ratio of 0·39 (theoretical 0·386) can be obtained by use of values deduced from the combination analysis of these two modes.

TABLE 4

Assignment of fundamental vibrations for C_5H_5NiNO and its D$_5$- and ^{15}NO-analogues

Species	No.	Description	Assignments C_5H_5NiNO	 C_5D_5NiNO	 $C_5H_5Ni^{15}NO$
A_1(I.r., R)	1	Sym. C–H stretch	3115 [a]	2335	3115
	2	N–O stretch	1809	1808	1774
	3	Sym. ring breath	1112	1052	1111
	4	Sym. C–H bend (‖)	799	600	799
	5	Ni–N stretch	649	649	642
	6	Ring-Ni stretch	322	298	321
A_2(Inactive)	7	C–H bend (⊥)	1240 [c]		
E_1(I.r., R)	8	C–H stretch	3105	2286	3105
	9	C–C stretch	1425	1296	1424
	10	C–H bend (‖)	1054	852	1054
	11	C–H bend (⊥)	1005	771	1005
	12	Ni–N–O bend	484	478	470
	13	Ring-Ni tilt	290	(275) [d]	290
	14	Ring-Ni–N bend	92	(92)	(92)
E_2(R)	15	C–H stretch	3098	(2286)	(3098)
	16	C–C stretch	1343	(1212)	(1343)
	17	C–H bend (‖)	1102 [c]	862 [c]	(1102)
	18	C–H bend (⊥)	964	(740)	(964)
	19	Ring distortion (⊥)	840	(766)	(840)
	20	Ring distortion (‖)	565	(533)	(565)

[a] All frequencies are taken from liquid i.r. and Raman spectra. [b] (‖) and (⊥) refer to vibrations parallel and perpendicular to the C_5 symmetry axis. [c] Observed in the solid state (ref. 12). [d] Values in parentheses deduced from combinations and overtones.

E_2 vibrations. These vibrations are Raman-active only under C_{5v} molecular symmetry. By comparison with the i.r. spectrum of liquid C_5H_5NiNO, the following assignments can be made: the peak at 3098 cm^{-1} is readily attributed to the E_2 C–H stretching mode. The line at 1343 cm^{-1} was not observed by Hyams and Lippincott[3] but appears in our Raman spectrum as a weak unpolarized absorption. Its intensity and position justify attribution to the E_2 C–C stretch.

The line at 964 cm^{-1} is attributed to the perpendicular E_2 C–H bending, also because it is definitely unpolarized. The lines at 840 and 565 cm^{-1} are tentatively assigned, according to Bailey,[11] as perpendicular and parallel ring distortions, respectively.

No line attributable to the E_2 parallel C–H bending mode can be found in the Raman spectrum. In our low-temperature i.r. spectrum,[12] however, an absorption at 1102 cm^{-1} becomes active (and moves to 864 cm^{-1} in the D$_5$-molecule). This band can be assigned as the E_2 parallel bending mode, since the H : D ratio is of the order expected for such a vibration.

Conclusions.—Only few changes to the earlier vibrational assignments for the C_5H_5NiNO molecule[2,3] are required. However, the present comparative analysis of the three isotopic species definitely substantiate previous studies, carried out only on the light compound.

Our analysis of the combination bands, made more reliable by use of isotopes, clearly shows that there is mixing of modes localized on both the organic and inorganic halves of the molecule. This suggests that caution must be exercised in using the 'local symmetry' approximation in complexes of this type.

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[11] R. T. Bailey, *Spectrochim. Acta*, 1971, **27**, *A*, 199.
[12] Unpublished results.