

Complexes of Iron and Cobalt Containing Coordinated Molecular Dihydrogen: Infrared Evidence for $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ in Liquefied Xenon Solution

Gerard E. Gadd,[†] Rita K. Upmacis, Martyn Poliakoff,* and James J. Turner*

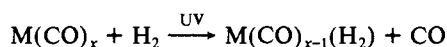
Contribution from the Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England. Received October 28, 1985

Abstract: $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ were generated by UV photolysis of $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $\text{Co}(\text{CO})_3(\text{NO})$ dissolved in liquefied xenon at -104°C and under 10–20 atm of pressure of H_2 or D_2 . Coordinated molecular dihydrogen and dideuterium were identified by $\nu(\text{H}-\text{H})$ ($\sim 3000\text{ cm}^{-1}$) and $\nu(\text{D}-\text{D})$ ($\sim 2200\text{ cm}^{-1}$) IR bands. Lower frequency IR bands associated with coordinated H_2 and D_2 are also reported. Both compounds decayed with pseudo-first-order kinetics in $t_{1/2} \sim 20\text{--}30\text{ min}$ at -104°C when the H_2 or D_2 was vented from the IR cell. Extensive additional IR data (available as supplementary material) are given for $\text{Fe}(\text{CO})_2(\text{NO})_2$, $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$, and H_2 and D_2 dissolved in liquefied xenon.¹⁸

There is considerable interest in how molecular hydrogen, H_2 , reacts with coordinatively unsaturated transition-metal centers. Until recently, such reactions were generally presumed to involve (1) the initial, albeit transient coordination of molecular dihydrogen to form an unstable complex and (2) the subsequent dissociation of the H–H bond to form stable dihydride compounds. This view has been somewhat changed by the isolation¹ of the first stable dihydrogen complexes, $\text{M}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$ ($\text{M} = \text{Mo}$ or W , $\text{R} = \text{cy}$ or $i\text{-Pr}$). Since then, there has been spectroscopic identification of several complexes,^{2–5} most rather less stable than the first, but all containing coordinated dihydrogen.

It is now important to ask what factors determine the relative stabilities of molecular dihydrogen compounds and metal dihydrides. In what circumstances can dihydrogen be coordinated by a metal center without cleavage of the H–H bond? All the dihydrogen complexes reported so far^{1–5,25} have involved metals with $d^4\text{--}d^6$ configuration. In this paper, however, we present detailed IR evidence for the formation, in liquid xenon solution, of two complexes, $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$, both of which have nominal d^{10} configurations.

Liquid xenon (LXe) has proved itself to be a very useful solvent for characterizing reactive and unstable transition-metal complexes.⁶ In particular, it provides a simple and general route to dihydrogen compounds,^{2,7} and photolysis of metal carbonyl in the presence of H_2 .



This route has been used to generate the complexes $\text{M}(\text{CO})_3(\text{H}_2)$ ($\text{M} = \text{Cr}$, Mo , and W), where the coordinated H_2 , HD, or D_2 could be identified by IR spectroscopy.^{2,7}

In this paper, (i) we show how IR spectra in the $\nu(\text{C}-\text{O})$ and $\nu(\text{N}-\text{O})$ regions can be used to monitor the generation of $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ and $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ in liquid xenon, (ii) we use diagnostic $\nu(\text{H}-\text{H})$ bands, $\sim 3000\text{ cm}^{-1}$, and their D_2 analogues, 2200 cm^{-1} , to confirm the presence of coordinated dihydrogen in both compounds, (iii) we demonstrate that IR bands below 1500 cm^{-1} also provide evidence for the coordination of H_2 and D_2 , (iv) we examine the thermal stability and decay of the two compounds, and (v) in the Discussion we summarize the evidence for the formation of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ and briefly discuss the bonding between H_2 and the metal centers in these complexes.

Experimental Section

The liquid Xe cell, originally designed by Maier et al., has been described in detail previously.⁸ It has 2.7-cm path length and 8.5-mL

volume. Liquid Xe has a number of advantages over solid matrices which have also been used^{3,4} for the generation of dihydrogen complexes: (i) much larger quantities of compound can be generated because of the greater path length in liquids and weak IR bands are more easily observed;² (ii) the reactant gases can be rapidly ($<5\text{ min}$) changed, from say H_2 to D_2 ; (iii) the temperature can be easily varied over the range -110°C (melting point of Xe) to -35°C . The experiments described in this paper were carried out at -104°C (169 K). However, matrices have one advantage over solutions, namely that polynuclear photoproducts are unlikely to be formed.

All IR spectra were obtained with a Nicolet MX 3600 interferometer and 1280 data system. Most interferograms were collected with 16K data points (2-cm^{-1} resolution). $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $\text{Co}(\text{CO})_3(\text{NO})$ were prepared by literature methods⁹ and were handled in a stainless steel vacuum line. Xe and H_2 (BOC Research Grade) and D_2 (BDH) were used without further purification. All photolysis was performed with a 250-W high-pressure Hg arc focused with quartz lenses.

In each experiment, the cell was partially filled with liquid Xe to obtain background spectra, the appropriate metal nitrosyl was added, the remainder of the cell was filled with liquid Xe, and the apparatus was finally pressurized with H_2 , normally to 10–15 atm. The liquid Xe was stirred during photolysis and usually during the recording of spectra. For both compounds, a "control" photolysis was carried out in the absence of H_2 to identify any photoproducts which did not involve H_2 . In the case of $\text{Fe}(\text{CO})_2(\text{NO})_2$, we observed a number of dimeric species in the control experiments¹⁰ which will be discussed separately.¹¹

IR bands have only been assigned to a particular species if it could be shown that the bands had constant relative intensities in a large number of different IR spectra. These data are presented graphically in great detail elsewhere.¹⁰ All reactions appear to take place with high quantum yields.

Results

Generation of $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$. Figure 1a shows the IR spectrum in the $\nu(\text{CO})$ and $\nu(\text{NO})$ regions of $\text{Co}(\text{CO})_3(\text{NO})$

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[†] Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

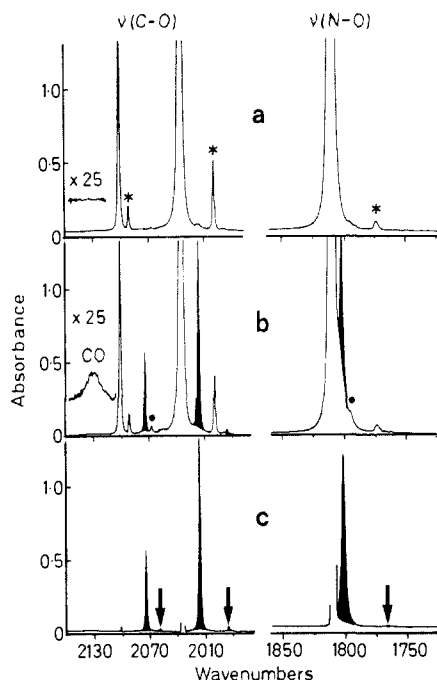


Figure 1. IR spectra in the $\nu(\text{C-O})$ and $\nu(\text{N-O})$ region illustrating the formation of $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ in liquid xenon (LXe) at -104°C under 10 atm of H_2 pressure: (a) before photolysis of $\text{Co}(\text{CO})_3(\text{NO})$; the bands marked with asterisks are due to molecules containing ^{13}C , ^{15}N , and ^{18}O in natural abundance; (b) after UV photolysis bands colored black are due to $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$; bands marked \bullet are due to small amounts of $\text{Co}(\text{CO})_2(\text{NO})(\text{N}_2)^{10,12}$ formed by reaction with trace impurities of N_2 (~ 1 ppm) in the LXe; (c) produced by computer subtraction showing the bands of $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$; arrows mark ^{13}C , ^{15}N , and ^{18}O satellites; see Tables I and II. Note that in a and b, there are inset spectra with $\times 25$ expansion of the absorbance scale to show the formation of CO during photolysis.

Table I. Observed and Calculated Band Positions (cm^{-1}) of the $\nu(\text{CO})$ and $\nu(\text{NO})$ Vibrations of $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$, in Liquid Xe at 169 K

obsd	calcd	assignment
2073.75		$a'\nu(\text{CO})$
2058.75	2058.53	$a'\nu(^{13}\text{CO})$
2015.25		$a''\nu(\text{CO})$
1984.31	1984.87	$a''\nu(^{13}\text{CO})$
1800.94		$a'\nu(\text{NO})$
1764.06	1768.63/1753.6	$a'\nu(^{15}\text{NO})/a'\nu(\text{N}^{18}\text{O})$

Table II. Factored Force Constants (N m^{-1}) for $\text{Co}(\text{CO})_3(\text{NO})$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ in Liquid Xe

	$\text{Co}(\text{CO})_3(\text{NO})$	$\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$
f_{CO}	1709.15	1688.77
$f_{\text{CO,CO}}$	37.37	48.31
f_{NO}	1441.29	1426.75

dissolved in liquid Xe at 169 K. The most intense bands are due to the $a_1 + e$ $\nu(\text{C-O})$ and a_1 $\nu(\text{N-O})$ vibrations, while the weaker bands marked with asterisks are due to $\text{Co}(\text{CO})_3(\text{NO})$ molecules containing natural abundance ^{13}CO , ^{15}NO , or N^{18}O . On UV photolysis, under 10 atm of H_2 pressure, three new intense bands, two $\nu(\text{C-O})$ and one $\nu(\text{N-O})$, appear. These bands are colored black in Figure 1b. The overall band pattern of the primary photoproduct is more easily seen in Figure 1c where computer subtraction has been used to remove absorptions due to unreacted $\text{Co}(\text{CO})_3(\text{NO})$. This pattern, one $\nu(\text{N-O})$ and two $\nu(\text{C-O})$ bands, is exactly what is expected for a $\text{Co}(\text{CO})_2(\text{NO})$ moiety. The assignment is confirmed by the natural abundance ^{13}CO satellites (arrowed in Figure 1c), which are observed precisely at the wavenumbers predicted by a simple C-O factored force field¹³

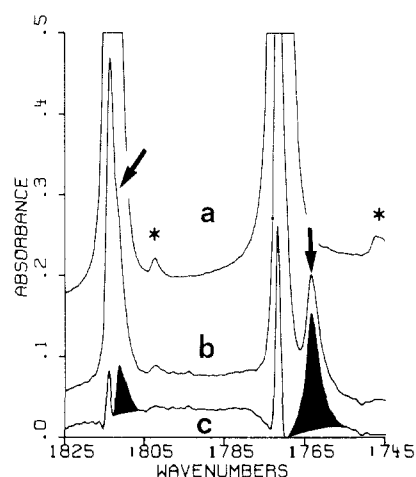


Figure 2. IR spectra in the $\nu(\text{N-O})$ region showing the photolytic formation of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ in LXe: (a) Bands of $\text{Fe}(\text{CO})_2(\text{NO})_2$ before photolysis; those marked with asterisks are due to natural abundance ^{15}N and ^{18}O ; (b) bands after UV photolysis; arrowed bands are due to $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$; (c) spectrum produced by computer subtraction; bands colored black are due to $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$; see Tables III and V.

Table III. $\nu(\text{CO})$ and $\nu(\text{NO})$ Band Positions (cm^{-1}) of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ in Liquid Xe at 169 K

obsd	calcd	assignment
2052		$a'\nu(\text{CO})$
2006.9	2006.25	$a'\nu(^{13}\text{CO})$
1811		$a'\nu(\text{NO})$
	1799.68 ^a	$a'(\nu(^{15}\text{NO})/\nu(\text{N}^{18}\text{O}))$
1763		$a''\nu(\text{NO})$
1738.4	1742.42 ^a	$a'(\nu(^{15}\text{NO})/\nu(\text{N}^{18}\text{O}))$

^a Calculated for $\nu(^{15}\text{N}^{16}\text{O})$.

Table V. Force Constants (N m^{-1}) for $\text{Fe}(\text{CO})_2(\text{NO})_2$, $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$, and $\text{Fe}(\text{N}_2)(\text{CO})(\text{NO})_2$

	$\text{Fe}(\text{CO})_2(\text{NO})_2^a$ in liq Xe	$\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)^a$ in liq Xe	$\text{Fe}(\text{N}_2)(\text{CO})(\text{NO})_2^b$ in liq Kr
f_{CO}	1714	1700.83	1690.9
$f_{\text{CO,CO}}$	40.97		
f_{NO}	1411.6	1405	1399
$f_{\text{NO,NO}}$	33.56	37.69	34.3

^a This work. ^b Reference 15.

(see Table I). During the photolysis, a very weak band due to free CO was observed to grow in at 2130 cm^{-1} .

Thus, in the presence of H_2 , a new product is formed by photolysis of $\text{Co}(\text{CO})_3(\text{NO})$. The formation involves loss of CO and the product is a $\text{Co}(\text{CO})_2(\text{NO})\text{L}$ compound. The frequency factored force constants of the product (Table II) are lower than those of $\text{Co}(\text{CO})_3(\text{NO})$, suggesting that the Co center in the product has not been significantly oxidized.

Generation of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$. The results of photolyzing $\text{Fe}(\text{CO})_2(\text{NO})_2$ in the presence of H_2 were broadly similar to those obtained with $\text{Co}(\text{CO})_3(\text{NO})$. The primary photoproduct has one $\nu(\text{CO})$ and two $\nu(\text{NO})$ bands, as expected for $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$. The spectra are slightly less clear than for the Co compound, because one of the $\nu(\text{NO})$ bands of the Fe product overlaps a band of the parent $\text{Fe}(\text{CO})_2(\text{NO})_2$ and can only be clearly seen after computer subtraction of the spectra, Figure 2. Since such computer subtractions can sometimes give rise to artifacts, it is important to have an independent confirmation of this band.

In the case of $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$, confirmation of two $\nu(\text{CO})$ bands could be gained from the natural abundance ^{13}CO satellites (Tables I and II). Unfortunately, we cannot use ^{15}NO satellites in a similar way for $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ because N-O factored

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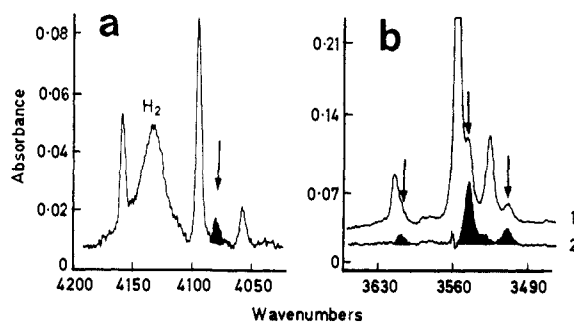


Figure 3. IR spectra in the first overtone regions: (a) spectrum in the $2\nu(\text{C-O})$ region, after UV photolysis of $\text{Fe}(\text{CO})_2(\text{NO})_2$ and H_2 in LXe at 169 K; unlabeled bands are due to unreacted $\text{Fe}(\text{CO})_2(\text{NO})_2$; the band colored black is due to $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$, and the band labeled H_2 is the Q_0 band¹⁸ of free H_2 dissolved in LXe; (b) spectra in the $2\nu(\text{N-O})$ region (1) spectrum of the same sample as spectrum a, with the bands due to $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ arrowed (2) after computer subtraction has been used to remove the bands of unreacted $\text{Fe}(\text{CO})_2(\text{NO})_2$; the bands colored black are due to $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$. Note that both the absorbance and wavenumbers are plotted on different scales in a and b.

Table X. Wavenumbers (cm^{-1}) of the Overtone/Combination $\nu(\text{CO})$ and $\nu(\text{NO})$ Bands of (A) $\text{Fe}(\text{CO})_2(\text{NO})_2$ and (B) $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ in Liquid Xe at 169 K

transition	symmetry (A, C_{2v} ; B, C_s)	expected (E)	obsd (O)	shift (O - E)
A				
$2(a_1\nu(\text{CO}))$	a_1	4168.8	4159.9	-8.9
$2(b_2\nu(\text{CO}))$	a_1	4070	4057.2	-12.8
$(a_1 + b_2)\nu(\text{CO})$	b_2	4119.4	4095.8	-23.6
$2(a_1\nu(\text{NO}))$	a_1	3625	3617.4	-7.6
$2(b_1\nu(\text{NO}))$	a_1	3540	3529.5	-10.5
$(a_1 + b_1)\nu(\text{NO})$	b_1	3582.5	3560.35	-22.15
$a_1\nu(\text{CO}) + a_1\nu(\text{NO})$	a_1	3896.9	3896.3	-0.6 v wk
$a_1\nu(\text{CO}) + b_1\nu(\text{NO})$	b_1	3854.4	3856.2	1.8 v wk
$b_2\nu(\text{CO}) + a_1\nu(\text{NO})$	b_2	3847.5	3849.5	2 v wk
$b_2\nu(\text{CO}) + b_1\nu(\text{NO})$	a_2 (IR forbidden)	3805		
B				
$2(a'\nu(\text{CO}))$	a'	4104	4080.9	-24
$2(a'\nu(\text{NO}))$	a'	3622	3611	-11
$2(a''\nu(\text{NO}))$	a'	3526	3508.75	-17.25
$(a' + a'')\nu(\text{NO})$	a''	3574	3549	-25

force fields are much less reliable than C-O factored,^{14,15} see Tables III and V. It was possible, however, to generate a sufficient concentration of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ to use the first overtone region of the IR spectrum, illustrated in Figure 3. In the $2\nu(\text{CO})$ region, $\text{Fe}(\text{CO})_2(\text{NO})_2$, which has two CO groups, shows three IR bands, consisting of two overtones ($2a_1$ and $2b_1$) and one combination ($a_1 + b_1$). On the other hand, the photoproduct, $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$, which has only one CO group, shows only one $2\nu(\text{CO})$ overtone band, colored black in Figure 3a. However, in the $2\nu(\text{NO})$ region, Figure 3b, both $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ have three bands. This confirms that like $\text{Fe}(\text{CO})_2(\text{NO})_2$, the photoproduct contains two NO groups. All frequencies are summarized in Table X and the anharmonicity constants are given in Table IV of the supplementary material.

Also shown in Figure 3a is a broad absorption, labeled H_2 , which is one of the absorptions due to molecular hydrogen dissolved in liquid Xe. Since neither H_2 nor D_2 has a permanent dipole moment, they might not be expected to have IR absorptions. However, absorption does occur through the dipole moment, induced by the so-called "solvent cavity" interacting with the molecular quadrupole moment of H_2 or D_2 . This gives rise to ab-

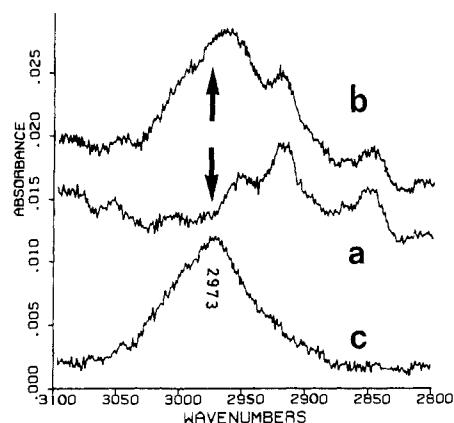


Figure 4. IR spectra illustrating the $\nu(\text{H-H})$ band of coordinated molecular dihydrogen in $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$: (a) spectrum before photolysis showing bands due to trace hydrocarbon impurities in the liquid Xe; (b) after photolysis of $\text{Fe}(\text{CO})_2(\text{NO})_2$ under 10 atm of H_2 pressure; (c) computer subtraction, spectrum b minus spectrum a.

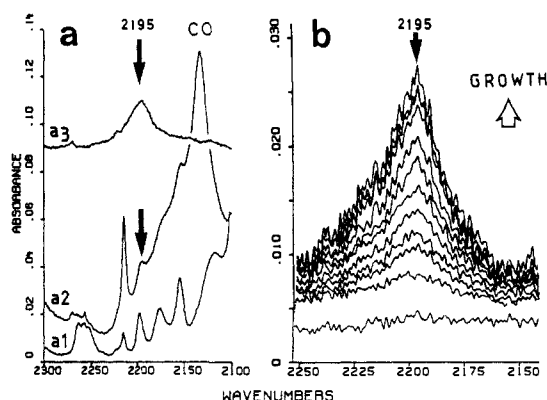


Figure 5. IR spectra illustrating the $\nu(\text{D-D})$ band of coordinated dideuterium in $\text{Fe}(\text{CO})(\text{NO})_2(\text{D}_2)$: (a1) spectrum before photolysis; all bands are overtone and combination bands of $\text{Fe}(\text{CO})_2(\text{NO})_2$; (a2) after photolysis; the strongest band is due to free CO in the solution, and the arrow indicates the very weak band associated with coordinated D_2 ; (a3) spectrum 2, after a sequence of computer subtractions to extract the band due to coordinated D_2 ; (b) series of spectra, each obtained by computer subtraction, showing the steady growth in intensity of the $\nu(\text{D-D})$ band of coordinated D_2 as the photolysis proceeds. Note that b is plotted with expanded absorbance and wavenumber scales relative to a.

sorptions by vibrational, rotational, and translational transitions. Such absorptions have been previously reported for H_2 and D_2 in cryogenic matrices¹⁶ and liquefied Ne,¹⁷ and we have observed eight bands due to H_2 and nine bands due to D_2 dissolved in liquid Xe.¹⁸ The importance of these absorptions in our experiments is that they can be used to monitor the dissolved gases and to ensure, for example, that H_2 has been successfully vented from solution before D_2 is added.

We now confirm the presence of coordinated molecular H_2 in $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ from IR bands in the $\nu(\text{H-H})$ and $\nu(\text{D-D})$ region.

$\nu(\text{H-H})$ and $\nu(\text{D-D})$ IR Bands. IR bands in the region $3100\text{--}2700\text{ cm}^{-1}$ appear to be characteristic of compounds containing coordinated dihydrogen.^{1,2,7} Figure 4 shows this region of the spectrum during photolysis of $\text{Fe}(\text{CO})_2(\text{NO})_2$ and H_2 in

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(18) The wavenumbers of these bands are all collected in Tables VIII and IX, available as supplementary material. These wavenumbers can be used to calculate values of the rotational constants for the vibrational ground state: B_0 for $\text{H}_2 = 58.59\text{ cm}^{-1}$ and B_0 for $\text{D}_2 = 29.32\text{ cm}^{-1}$; D_0 for $\text{H}_2 = 0.0418\text{ cm}^{-1}$ and D_0 for $\text{D}_2 = 0.0012\text{ cm}^{-1}$.

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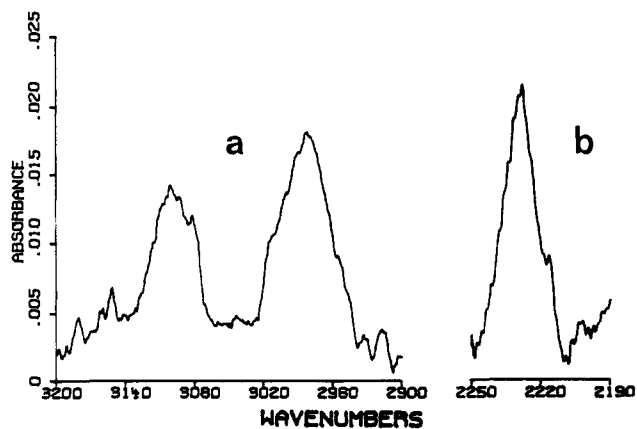


Figure 6. (a) Bands assigned to $\nu(\text{H-H})$ of coordinated H_2 in $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$. (b) $\nu(\text{D-D})$ of coordinated D_2 in $\text{Co}(\text{CO})_2(\text{NO})(\text{D}_2)$. Note that the two spectra were obtained at different stages of the experiment. The bands in spectrum a have been extracted by computer subtraction (cf. Figure 4) and have been digitally smoothed. Spectrum b is plotted on twice the wavenumber scale of spectrum a.

liquid Xe. Before photolysis, spectrum 4a, there were some weak absorptions due to trace hydrocarbon impurities. During UV photolysis, a broad absorption grew in at 2973 cm^{-1} , spectrum 4b. This absorption was somewhat clearer when the hydrocarbon absorptions has been removed by computer subtraction, spectrum 4c. The band belonged to the same species as the $\nu(\text{CO})$ and $\nu(\text{NO})$ bands discussed above, because it shows exactly the same pattern of growth and decay of intensity. Thus we have a band, 2973 cm^{-1} , exactly in the region expected for $\nu(\text{H-H})$ of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$, containing coordinated molecular H_2 .

When $\text{Fe}(\text{CO})_2(\text{NO})_2$ was photolyzed under a pressure of D_2 , the band at 2973 cm^{-1} was not observed. $\text{Cr}(\text{CO})_5(\text{D}_2)$ has a $\nu(\text{D-D})$ absorption at 2242 cm^{-1} in liquid Xe² compared to 3030 cm^{-1} for $\text{Cr}(\text{CO})_5(\text{H}_2)$, a frequency ratio of 1.35. By analogy one might expect $\text{Fe}(\text{CO})(\text{NO})_2(\text{D}_2)$ to have a $\nu(\text{D-D})$ absorption at $\sim 2200\text{ cm}^{-1}$ (i.e., $2973/1.35\text{ cm}^{-1}$). Unfortunately, this region was quite congested with weak overtone and combination bands, even before photolysis, Figure 5a1. After photolysis, the spectrum was dominated by the absorption of free CO, Figure 5a2. However, there was a weak shoulder, arrowed, which could be extracted by a careful sequence of computer subtractions to remove the overtones, free CO, etc., to reveal a band at 2195 cm^{-1} , Figure 5a3. During the UV photolysis, 10 IR spectra were recorded, the computer subtraction showed this IR band at 2195 cm^{-1} steadily growing in intensity, Figure 5b, and the rate of growth exactly paralleled that of other weak absorptions of $\text{Fe}(\text{CO})(\text{NO})(\text{D}_2)$. Similarly, during the thermal decay of $\text{Fe}(\text{CO})(\text{NO})_2(\text{D}_2)$, which occurred after the pressure of D_2 was vented, this band decreased at the same rate as the other bands of $\text{Fe}(\text{CO})(\text{NO})_2(\text{D}_2)$ (not illustrated). Thus, the band appears to be a genuine absorption of $\text{Fe}(\text{CO})(\text{NO})_2(\text{D}_2)$ and not merely a fortuitous artifact of computer subtraction.

Both of the $\nu(\text{H-H})$ and $\nu(\text{D-D})$ IR absorptions are extremely broad: the $\nu(\text{H-H})$ band, 75 cm^{-1} fwhm, and the $\nu(\text{D-D})$ band, $\sim 35\text{ cm}^{-1}$ fwhm. These half-widths are almost exactly twice those observed²⁷ for $\text{Cr}(\text{CO})_5(\text{H}_2)$, 38 cm^{-1} , and $\text{Cr}(\text{CO})_5(\text{D}_2)$, 16 cm^{-1} , at the higher temperature of $-74\text{ }^\circ\text{C}$. In the Cr compound, the broadness has been tentatively ascribed to rotation about the M-H₂ axis.⁷ Possibly, the increased line widths for Fe reflect a lower barrier to rotation. It is also interesting to note that the line widths of H_2 coordinated to Fe are similar to those of uncoordinated H_2 dissolved in liquid Xe; see Figure 3a.

The photolysis of $\text{Co}(\text{CO})_3(\text{NO})$ and D_2 produced a band at 2228 cm^{-1} , which was well-resolved without any computer subtraction, Figure 6b. Somewhat surprisingly, after the photolysis of $\text{Co}(\text{CO})_3(\text{NO})$ and H_2 , two absorptions appeared in the $\nu(\text{H-H})$ region, Figure 6a. These bands both appear to belong to $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$. The expected position for $\nu(\text{H-H}) \sim 3010\text{ cm}^{-1}$ (i.e., $2228 \times 1.35\text{ cm}^{-1}$) lies between the two observed bands 3100 and 2976 cm^{-1} , and the splitting may well be due to a fortuitous

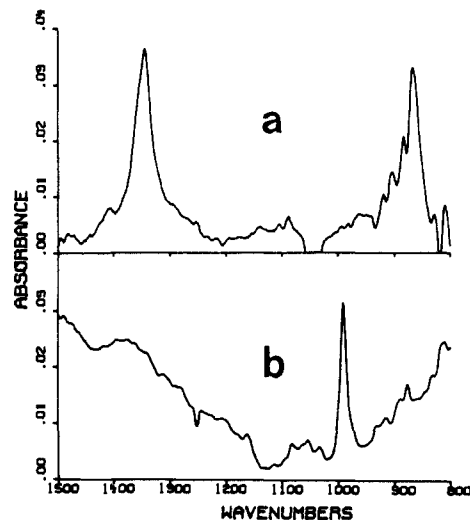


Figure 7. Lower frequency IR bands of (a) $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ and (b) $\text{Co}(\text{CO})_2(\text{NO})(\text{D}_2)$. In both cases, bands due to unreacted $\text{Co}(\text{CO})_3(\text{NO})$ have been removed by computer subtraction.

Table XI. Wavenumbers of IR Bands Associated with Vibrations of Coordinated Dihydrogen and Dideuterium

	$\text{Fe}(\text{CO})_2(\text{NO})_2(\text{H}_2)^a$	$\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)^a$	$\text{W}(\text{CO})_3(\text{Pcy}_3)_2(\text{H}_2)^b$
$\nu(\text{H-H})$	2973	{ 3100 } { 2976 }	2690
$\nu(\text{D-D})$	2195	2228	$\sim 1900^c$
$\nu(\text{M-H}_2)$ antisym	1374	1345	1570
$\nu(\text{M-D}_2)$ antisym	1003	991	1132
$\nu(\text{M-H}_2)$ sym	$\sim 870^d$	868	953
$\nu(\text{M-D}_2)$	<i>e</i>	<i>e</i>	703

^a This work, liquid Xe, $-104\text{ }^\circ\text{C}$, 169 K. ^b Reference 1, Nujol mull, room temperature. ^c Observed only in Raman spectrum. ^d This area is somewhat complicated by overtones of lower frequency vibrations—the M-H₂ band cannot be completely resolved even when using spectral subtraction. ^e Not observed.

Fermi resonance with overtones and combination of lower frequency vibrations; see next section.

Other Bands Associated with Coordinate H_2 . Both $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ and $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ have IR bands apparently associated with stretching of the M-H bonds in a triangular unit. The bands all shift in frequency on deuteration. This is illustrated for $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ in Figure 7, and all the data are collected in Table XI. The frequencies of these bands are too low to be due to M-H stretching vibrations of a metal dihydride. The bands are indeed substantially lower in frequency than the bands assigned to the symmetric and antisymmetric M-(H₂) stretching vibrations¹ of $\text{W}(\text{CO})_3(\text{Pcy}_3)_2(\text{H}_2)$; see Table XI. These lower frequencies appear to be consistent with the rather lower thermal stability of the nitrosyl dihydrogen complexes.

Thermal Decay of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$. Under a pressure of H_2 , 10–20 atm, both $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ were stable in liquid Xe at 169 K over a period of several hours. When the H_2 pressure was vented and the cell repressurized with D_2 , exchange of coordinated H_2 and D_2 occurred before the first IR spectra could be recorded (i.e., within 5 min). This contrasts sharply with $\text{Cr}(\text{CO})_5(\text{H}_2)$ where H_2/D_2 exchange occurs more slowly even at considerably higher temperature,⁷ i.e., $t_{1/2} \sim 30\text{ min}$ at 200 K.

When the H_2 or D_2 pressure was vented and no other gases were added, $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ decayed by good first-order kinetics, Figure 8. It can be seen from this figure that the rates of decay are similar for the two compounds.¹⁹ In

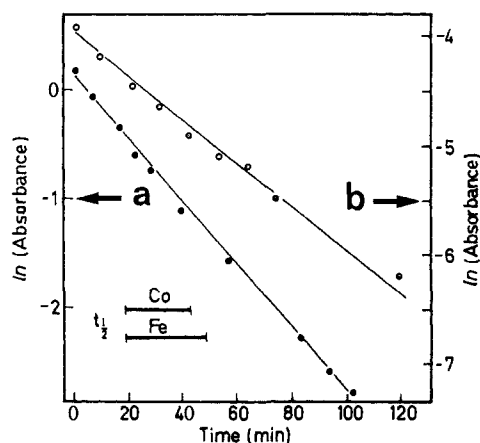


Figure 8. Plots of \ln (IR absorbance) vs. time, showing the pseudo-first-order decay of (a) $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ and (b) $\text{Fe}(\text{CO})(\text{NO})_2(\text{D}_2)$ ¹⁹ in liquid Xe at -104°C (169 K) after the pressure of H_2 or D_2 was vented from the cell. The IR bands used to monitor the decay were $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$, 1800.9 cm^{-1} (see Table I), and $\text{Fe}(\text{CO})(\text{NO})_2(\text{D}_2)$, 1003 cm^{-1} (see Table XI). The solid bars indicate the approximate half-lives of the two decays.

the case of Co, both $\text{Co}(\text{CO})_3(\text{NO})$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{N}_2)$ ¹² could be detected as decay products, although the dinitrogen compound was itself thermally unstable and decayed further. For the decay of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$, the regeneration of the parent $\text{Fe}(\text{CO})_2(\text{NO})_2$ was greater than 80% as monitored by the growth of the ^{13}CO satellites; see Table III.

It is not clear whether these first-order kinetics represent dissociative or associative pathways for decays, or even a combination of both, as has been found for substitution in the parent nitrosyl species.²⁰ For our present work, there are two significant features of the thermal decay. (1) There is no evidence for the formation of a metal dihydride species; decay merely involves loss of H_2 and recombination with CO, overall the inverse of photolysis. (2) The Fe and Co complexes have similar thermal stabilities but appear to be rather less stable than the d^6 metal complexes,^{2,7,21} $\text{M}(\text{CO})_5(\text{H}_2)$.

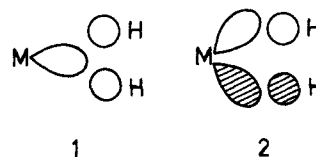
Discussion

Evidence for Complexes with Coordinated Molecular Dihydrogen. Before discussing the bonding of H_2 in $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$, we summarize the evidence for the compounds containing coordinated dihydrogen.

Both $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $\text{Co}(\text{CO})_3(\text{NO})$ form new compounds when photolyzed under a pressure of H_2 in liquid Xe. Formation of these compounds involves loss of CO and does not occur in the absence of H_2 . When the pressure of H_2 is vented, the compounds rapidly decay to regenerate the parent nitrosyl compounds. The $\nu(\text{CO})$ and $\nu(\text{NO})$ bands confirm the overall number of coordinated CO and NO groups, and the associated force constants suggest no oxidation of the transition-metal center. Both compounds have IR bands which display H_2/D_2 isotope shifts, close to those predicted for isolated H_2 and D_2 . There are no bands assignable to vibrations of metal hydrides, i.e., species in which the H-H or D-D bonds have been broken on coordination. There are, however, bands at $\sim 2200\text{ cm}^{-1}$ assignable to $\nu(\text{D}-\text{D})$ of coordinated D_2 and at $\sim 3000\text{ cm}^{-1}$ due to $\nu(\text{H}-\text{H})$ of coordinated H_2 , though for $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$ the $\nu(\text{H}-\text{H})$ absorption is split into two. Lower frequency vibrations are consistent with the symmetric and antisymmetric M-H stretching vibrations of the triangular group. There is no evidence to show whether H_2 is coordinated exactly symmetrically, but the broadness of the IR

bands suggests that the H_2 may be rotating freely.

Bonding of H_2 to Metals. There have been a number of recent theoretical studies on the reaction between H_2 and coordinatively unsaturated metal centers.²² Overall, a delicate balance between σ and π interactions, such as **1** and **2**, seems to determine whether coordination of H_2 to a particular metal center results in cleavage of the H-H bond. In principle, π interactions would be expected



to be strong for metals with eight or more d electrons, and so these metal should cleave the H-H bond. Thus, for example, d^8 species such as $\text{Fe}(\text{CO})_4$ ²³ are known to react with H_2 to form metal dihydrides.

Our work shows that both $\text{Fe}(\text{CO})(\text{NO})_2$ and $\text{Co}(\text{CO})_2(\text{NO})$ form dihydrogen complexes rather than dihydrides. These observations are surprising because the metals have a nominal d^{10} electronic configuration, where π interactions might have been expected to break the H-H bond. There are, unfortunately, too few dihydrogen complexes to generalize our observations which do, however, carry the implication that the NO group reduces the π -donor properties of the metal center and prevents cleavage of the H-H bond. It is now clearly important to study nitrosyl species with d^8 centers, e.g., $\text{Mn}(\text{CO})_3(\text{NO})$ and $\text{Cr}(\text{CO})_2(\text{NO})_2$, to see how these react with H_2 . Similarly, do d^{10} carbonyl species without nitrosyl groups, e.g., $\text{Ni}(\text{CO})_3$, form dihydrides?²⁴

Finally, it is worth noting that dihydrogen compounds seem to have properties similar to those of N_2 complexes. Those transition-metal fragments which have so far been shown to form H_2 complexes are also those which form dinitrogen complexes with relatively high $\nu(\text{N}\equiv\text{N})$ stretching frequencies, i.e., above 2150 cm^{-1} . This again indicates that a relatively poor π -donor system is required to avoid breaking the H-H bond.

Conclusions

Our experiments again demonstrate the versatility of liquefied Xe. This solvent provides general synthetic routes to particular classes of unstable complexes and permits extremely detailed spectroscopic studies of the complexes once formed. In this paper, we have extended the range of transition metals known to coordinate molecular dihydrogen. It is our belief that as in the case of "agostic C-H interactions", molecular dihydrogen complexes will be found to be very much more widespread than was originally thought.²⁵ Many hydrogenation reactions, particularly photocatalytic reactions with metal carbonyls,²⁶ may well involve the formation of dihydrogen complexes rather than metal dihydrides as the important catalytic intermediates.

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Registry No. $\text{Fe}(\text{CO})_2(\text{NO})_2$, 13682-74-1; $\text{Co}(\text{CO})_3(\text{NO})$, 14096-82-3; $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$, 101348-79-2; $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$, 101348-80-5; H_2 , 1333-74-0; D_2 , 7782-39-0.

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Supplementary Material Available: Further IR spectroscopic data of harmonic $\nu(\text{C-O})$ and $\nu(\text{N-O})$ frequencies and anharmonicity constants for $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ (Table IV), lower frequency ($>300 \text{ cm}^{-1}$) IR bands of $\text{Fe}(\text{C-}$

$\text{O})_2(\text{NO})_2$ (Table VI) and $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ (Table VII), and IR bands of H_2 (Table VIII) and D_2 (Table IX) dissolved in liquid Xe^{18} (7 pages). Ordering information is given on any current masthead page.

Microwave Spectra, Electric Dipole Moment, and Molecular Structure of *cis,trans*-1,2,3-Trifluorocyclopropane

R. N. Beauchamp, J. W. Agopovich,¹ and C. W. Gillies*

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180. Received August 22, 1985

Abstract: The microwave spectra of the normal, monodeuterated, dideuterated, and carbon-13 isotopic species of *cis,trans*-1,2,3-trifluorocyclopropane and *cis,trans*-1,2,3-trifluorocyclopropane-*d*₃ have been investigated and assigned in the region 26.5–40.0 GHz. The spectral assignments have yielded data sufficient for the complete determination of the molecular geometry in both the normal and trideuterated isotopic species frameworks. The partial r_s parameters in the normal isotopic species framework are $r(\text{C}_{1,2}\text{C}_3) = 1.478$ (10) Å, $r(\text{C}_1\text{C}_2) = 1.500$ (3) Å, $r(\text{C}_{1,2}\text{H}) = 1.076$ (6) Å, $r(\text{C}_3\text{H}) = 1.085$ (16) Å, $r(\text{C}_{1,2}\text{F}) = 1.367$ (8) Å, $r(\text{C}_3\text{F}) = 1.387$ (8) Å, $\theta(\text{HC}_{1,2}\text{F}) = 109.4$ (8)°, and $\theta(\text{HC}_3\text{F}) = 114.7$ (15)°, where atom C₃ lies in the *ac* symmetry plane of the molecule. All the ring bonds in the *cis,trans* isomer have shortened relative to cyclopropane, with the greater reduction occurring in the two equivalent *trans* ring bonds. The C–F bond distances are found to be inequivalent, with the longer C–F bond occurring in the HCF moiety exclusively *trans* to neighboring HCF groups. These results are interpreted in the context of several theoretical studies that predict the effect of fluorine substitution on the geometries of substituted cyclopropanes and oxiranes.

A number of experimental^{2–7} and theoretical^{8–12} studies have been undertaken to elucidate the effect of fluorine substitution on the geometries of fluorinated cyclopropanes and oxiranes. A portion of the theoretical work suggests that the ring bond changes observed in 1,1-difluorocyclopropane² and *cis,trans*-1,2,3-trifluorocyclopropane⁴ and the contraction of the C₁–C₂ bond in 1,1,2,2-tetrafluorocyclopropane³ relative to cyclopropane may be rationalized by fluorine-induced charge redistribution in occupied molecular orbitals (MOs) and the resultant forces acting on the ring nuclei.⁸ Several of the studies^{9,10} further suggest that the greater stability in the *trans* isomer of the *cis*- and *trans*-1,2-difluorocyclopropanes¹³ and the shorter C–C bond distance in the *trans* isomer of the *cis*- and *trans*-1,2-difluorooxiranes^{5,6} may derive from greater conjugative destabilization^{14,15} in the corresponding *cis* forms.

In the present study, the microwave investigation of various isotopic species of *cis,trans*-trifluorocyclopropane^{16,17} (Figure 1)

has yielded data sufficient for the complete determination of the molecular geometry of the compound in each of two different frameworks. Coordinates have been calculated in a number of ways and the results intercompared to establish the reliability of the parameters resulting.¹⁸ Trends in the experimentally determined ring geometries of the 1,2-difluorocyclopropanes^{19,20} and 1,2-difluorooxiranes^{5,6} have been identified and related to the observed ring geometry in *cis,trans*-1,2,3-trifluorocyclopropane in a manner consistent with available theory. Substituent orientation has been examined in several ring systems and the observations correlated with substituent orientation in *cis,trans*-1,2,3-trifluorocyclopropane to provide insight into angular effects observed in that species.

Experimental Section

Synthesis. (1) $\overline{\text{C}_1\text{HFC}_2\text{HFC}_3\text{FH}}$. The normal isotopic species of *cis,trans*-1,2,3-trifluorocyclopropane was synthesized by ozonolysis of 3 mmol of *trans*-1,2-difluoroethylene at -95°C in 3 mL of CF_3Cl , as described previously.^{17,21}

(2) $\overline{\text{C}_1\text{DFC}_2\text{DFC}_3\text{FD}}$. The *d*₃ isotopic species was synthesized by ozonolysis of 0.75 mmol of *trans*-1,2-difluoroethylene-*d*₂ at -95°C in 2 mL of CF_3Cl .

(3) $\overline{\text{trans-C}_1\text{DFC}_2\text{HFC}_3\text{FH}}$ and $\overline{\text{trans-C}_1\text{DFC}_2\text{HFC}_3\text{FD}}$. These isotopic species were synthesized by ozonizing an equimolar mixture of 1.6 mmol of *trans*-1,2-difluoroethylene-*d*₀ and *d*₂ at -95°C in 2 mL of CF_3Cl .

(4) $\overline{\text{cis-C}_1\text{HFC}_2\text{HFC}_3\text{FD}}$ and $\overline{\text{cis-C}_1\text{DFC}_2\text{DFC}_3\text{FH}}$. These isotopic

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