

INFRARED SPECTRUM OF $Mn(CO)_4NO$ IN THE SOLID STATE. FURTHER EVIDENCE FOR A C_{2v} MOLECULAR SYMMETRY

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SUMMARY

The infrared crystal spectrum of nitrosyltetracarbonylmanganese has been investigated at low temperature with polarized radiation. The results give additional support to the view that the molecule belongs to the C_{2v} point group, and seem to indicate that the most probable space group is $C_s^4 - Cc$.

INTRODUCTION

The molecular symmetry of the pseudo pentacarbonyliron complex, nitrosyltetracarbonylmanganese, is still a matter of controversy^{1,2,3}. Since it is well established that the molecule has a trigonal bipyramidal geometry, its symmetry depends, of course, on the position of the NO heteroligand with respect to the equatorial plane of the bipyramid.

From the solution infrared spectrum, in the carbonyl stretching region, Treichel *et al.*¹ deduced that the molecule must have a C_{3v} symmetry, with the NO group at an axial position. However, the X-ray determination of the crystal structure of $Mn(CO)_4NO$ by Frenz *et al.*², points to a NO group lying in the equatorial plane, giving the molecule a two-fold molecular and crystallographic symmetry axis.

Frenz and his colleagues hold the view that the vibrational levels of the carbonyl stretching modes in the infrared spectrum could be accidentally coincident, also having molecular C_{2v} symmetry; consequently only three C-O absorption bands would appear as reported¹. This argument is, in principle, spectroscopically acceptable if one assumes that the nitrosyl group only just removes the D_{3h} symmetry proper of pentacoordinated molecules such as pentacarbonyliron, of which the present manganese compound is an analog*.

It is well known that in the solid state, mostly at low temperature, the vibrational spectra of molecules give sharper and better resolved absorption bands. In

* Such a view is supported also by the fact that it is very difficult to distinguish crystallographically between reflections due to the NO group and those arising from the CO groups; the statistical positions of the ligands in the equatorial plane were therefore taken² as 2/3 C and 1/3 N.

addition, accidental and/or true degeneracy of vibrational levels can be removed owing to static crystal field and intermolecular coupling effects. In order to establish the true molecular symmetry of $\text{Mn}(\text{CO})_4\text{NO}$, we have undertaken a vibrational study on the crystal with the aid of polarized infrared radiation. This study is related to previous work from our laboratory on similar metal-carbonyl and -nitrosyl complexes in the crystalline state⁴⁻⁶.

EXPERIMENTAL

Nitrosyltetracarbonylmanganese was prepared from $\text{HMn}(\text{CO})_5$ and *N*-methyl-4-nitroso-*p*-toluene sulfonamide in ether solution by the method of Treichel *et al.*¹. The sample was distilled *in vacuo* before the spectra were recorded.

The measurements were carried out with Perkin-Elmer mod. 521, 225 and Beckman IR11 grating spectrometers. Wave-number calibration was against indene and water vapour peaks, and frequency values are accurate to $\pm 0.3 \text{ cm}^{-1}$.

Spectra of vapor, liquid, solution and solid phases were recorded with cells equipped with CsI windows. The solid state spectra were measured either with samples obtained by condensing vapor on cold CsI sheets, or with polycrystalline oriented films obtained by freezing the liquid. Repeated annealing was carried out on both types of solid sample before measurements. Spectra were taken in the temperature range

TABLE 1

IR FREQUENCIES OF $\text{Mn}(\text{CO})_4\text{NO}$ IN DIFFERENT PHASES

Vapor	Liquid	Solution	
		CH_3CN	CCl_4
P-Q-R { 2106.4 2102.0 m 2098.0 2087 (sh) 2038.0	2099 m	2100 m	2096 m 2086 (sh)
P-Q-R { 2034.4 vs 2029.8	2014 vs	2026 vs	2023 vs
P-Q-R { 1993.7 1989.0 vs 1985.4	1960 vs	1969 vs	1973 vs
P-Q-R { 1962.5 1957.6 mw 1953.6			1944 mw
P-Q-R { 1774.4 1767.0 vs 1763.4	1750 vs	1754 vs	1760 vs
656 s	648 s	656 s	655 vs
646 (sh)	641 (sh)	649 (sh)	647 (sh)
549 vw	546 vw		554 vw
526 s	524 s	524 s	525 s
456 s	454 vs	458 s	456 vs
394 w	396 w		399 w
361 w	361 w		360 w

between 250 and 100 K, and it was observed that no spectral modification was present.

The degree of crystal orientation was checked by placing the low temperature cell between crossed polaroids. A Perkin-Elmer gold wire grid-polarizer unit was used for the measurements with polarized radiation.

RESULTS AND DISCUSSION

The frequencies of the absorption bands for vapor, liquid and solution spectra are listed in Table 1. The classifications of the 27 fundamental modes, and their approximate descriptions assuming both C_{3v} and C_{2v} molecular symmetries are shown in Table 2.

In the region $2150\text{--}1900\text{ cm}^{-1}$, the solution spectra show four or five peaks according to the nature of the solvent. Four bands are observed in CH_3CN and other polar media, whereas five bands appear with non-polar solvents such as CS_2 and CCl_4^* . There are also five peaks in the liquid and vapor spectra, the absorption at 2087 cm^{-1} occurring as an ill-resolved shoulder. Since the absorptions at 2103, 2034 and 1991 cm^{-1} are attributed to C-O stretching modes¹ and, in our opinion, the 1942 cm^{-1} one is the $^{13}\text{C}\text{--O}$ mode, the nature of the 2087 cm^{-1} absorption remains to be established. Such a peak could be (i) the fourth C-O stretching fundamental, expected for a C_{2v} symmetry, (ii) a further $^{13}\text{C}\text{--O}$ satellite peak or, (iii) a hot band or a combination mode.

Moments of inertia have been calculated, using the molecular parameters from ref. 2, and $\text{Mn}(\text{CO})_4\text{NO}$ is found to be a prolate symmetric-top. Unfortunately, the separation of the P-R branches of the carbonyl bands did not allow any conclusions to be drawn as to the possible molecular symmetry. In fact, the difference between calculated value for C_{3v} and C_{2v} symmetries, found using the procedure of Seth-Paul⁸, is negligible. Furthermore, the experimental values are remarkably different from those calculated**.

TABLE 2

Approximate mode description	C_{3v} (IR activity: $A_1 + E$)	C_{2v} (IR activity: $A_1 + B_1 + B_2$)
C-O str.	$2A_1 + E$	$2A_1 + B_1 + B_2$
N-O str.	A_1	A_1
Mn-C str.	$2A_1 + E$	$2A_1 + B_1 + B_2$
Mn-N str.	A_1	A_1
Mn-N-O bend	E	$B_1 + B_2$
Mn-C-O bend	$A_1 + A_2 + 3E$	$2A_1 + 2A_2 + 2B_1 + 2B_2$
C-Mn-C	$A_1 + 3E$	$2A_1 + A_2 + 2B_1 + 2B_2$
N-Mn-C	$A_1 + 3E$	$2A_1 + A_2 + 2B_1 + 2B_2$

* Such a solvent effect is exactly the same as that previously observed in our laboratory for analogous complexes⁷.

** P-R separations, calculated using molecular parameters from ref. 2, are: for C_{3v} symmetry 9.08 cm^{-1} (\parallel); 9.81 cm^{-1} (\perp). For C_{2v} symmetry 9.06 cm^{-1} (\parallel , A); 9.72 cm^{-1} (\perp , B); 9.76 cm^{-1} (\perp , C).

Inspection of the spectrum between $700\text{--}600\text{ cm}^{-1}$, where $\nu(\text{Mn-N})$ and $\delta\text{-(Mn-N-O)}$ vibrations are expected, shows that in this region also, the number of observed absorptions is two or three (the first compatible with C_{3v} , the second with C_{2v} symmetry), according to the solvent used. Two bands are found in CH_3CN and other polar solvents, as before.

In conclusion, the results obtained from the spectra of the complex in the vapor, liquid and solution phases do not allow an unambiguous choice of molecular symmetry to be made, nor an assignment of the absorption bands observed to be carried out.

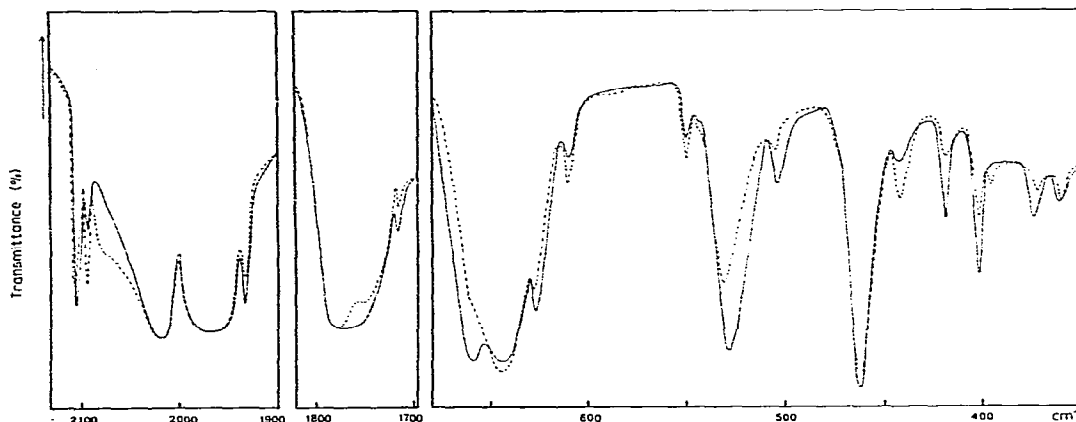


Fig. 1. Infrared crystal spectrum in polarized light of $\text{Mn}(\text{CO})_4\text{NO}$. Solid line: $\vec{E} \parallel$ to the slit direction. Dotted line: $\vec{E} \perp$ to the slit direction.

TABLE 3

INFRARED SPECTRUM OF CRYSTALLINE $\text{Mn}(\text{CO})_4\text{NO}$

Frequencies (cm^{-1})	Polarization ^a	Frequencies (cm^{-1})	Polarization
{ 2102.2 m	α	{ 551.2 w	β
{ 2100.0 m	β	{ 550 mw	α
{ 2088.8 mw	α	{ 530.2 s	β
{ 2088.0 w	β	{ 528.3 vs	α
2075 w	α	504 w	$\beta > \alpha$
2014 vs	$\alpha \approx \beta$	461 vs	$\beta \approx \alpha$
1964 vs	$\alpha \approx \beta$	{ 442.0 mw	β
1939 w	$\alpha \approx \beta$	{ 440.4 w	α
1774 vs	α	{ 418.5 w	α
1760 vs	β	{ 417.2 mw	β
1756 (sh)	α	401 m	$\beta \gg \alpha$
1708 w	$\alpha \approx \beta$	395 w	α
661 vs	$\beta \gg \alpha$	{ 372 w	β
645 vs	$\beta \approx \alpha$	{ 371 mw	α
{ 630.5 w	α	359 w	$\beta \approx \alpha$
{ 629.2 w	β		
{ 610.2 vw	β		
{ 609 w	α		

^a α = perpendicular polarized radiation; β = parallel polarized radiation

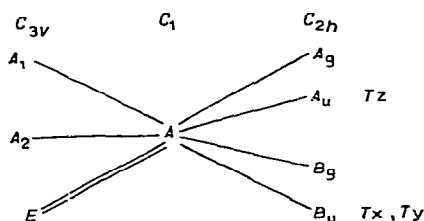
Since the data from the crystal spectrum (see Fig. 1 and Table 3) in polarized light seem to be more revealing in establishing the true molecular symmetry of $\text{Mn}(\text{CO})_4\text{NO}$, the discussion which follows is mainly centred on this spectrum.

Between 2200 and 1900 cm^{-1} five well defined absorptions are present. The band at higher frequency is a doublet with components at 2102 (\perp) and 2100 cm^{-1} (\parallel) showing a definite dichroic behaviour. The badly resolved shoulder at 2087 cm^{-1} in the vapor, becomes a rather intense band in the solid state spectrum. Furthermore, its two components at 2088.8 (\perp) and at 2088.0 (\parallel) show remarkable dichroic effects. The remaining three bands at 2014, 1964 and 1930 cm^{-1} seem to be unpolarized, except the 2014 cm^{-1} absorption, which shows a quite evident shoulder at 2075 cm^{-1} when the electric vector is perpendicular to the slit direction. Moreover the 1964 peak is a very broad structureless absorption in which a multiphonon process is probably involved. The N–O stretching band, at 1767 cm^{-1} in the vapor, shows some complexity in the crystal spectrum. In particular, when the electric vector of polarized radiation is perpendicular to the slit direction, two components at 1774 and 1756 cm^{-1} are observed. By contrast, with the parallel electric vector, the absorption appears as a broad intense singlet centred at 1760 cm^{-1} .

Below 700 cm^{-1} there are more absorptions in the solid state spectrum than in other phases. Between 700 and 600 cm^{-1} , a broad and intense band with components at 645, 630, 609 cm^{-1} (\perp) and 661, 645, 629, 610 cm^{-1} (\parallel), is present. Bands below 600 cm^{-1} show more remarkable dichroic effects. The peaks at 550 and 441 cm^{-1} have a clear doublet structure, with the perpendicularly polarized component more intense than the parallel one. Absorptions at 529, 418 and 372 cm^{-1} are also doublets, but with dichroic behaviour reversed with respect to the previous bands. The peak at 401 cm^{-1} is a strongly polarized singlet. The remaining absorptions at 461 and 359 cm^{-1} are unpolarized.

The above results point out that almost all the infrared bands have in the solid state spectrum a doublet with a small separation ($< 2 \text{ cm}^{-1}$) between the two components and the dichroic ratio is very high for many doublets.

The data allow a definite choice of the molecular symmetry to be made. In fact, if the molecule were of C_{3v} point group, since the symmetry of the unit cell is $C_{2h}^6 - C2/c$ the crystal spectrum should be interpretable on the basis of the following correlation chart:

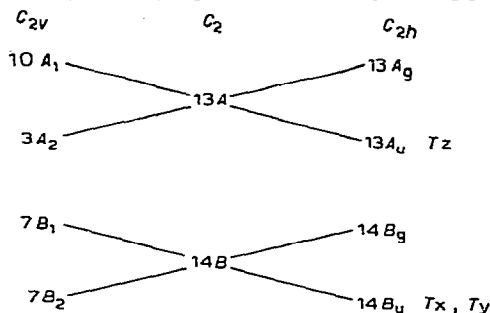


(Site group C_1 is used because there are no other sub-groups between the molecular group and the factor group)⁹.

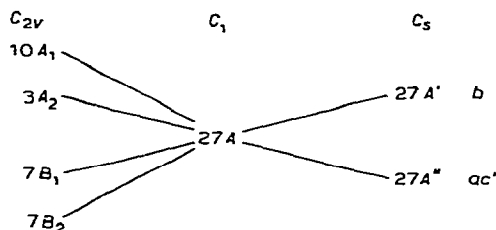
According to this scheme, the degenerate vibrations of the free molecule should split into two components owing to symmetry lowering in the crystalline site. The extent of such a site splitting cannot be predicted theoretically, but should be not very

different from those ($8\text{--}10\text{ cm}^{-1}$) found in similar carbonyl complexes^{4,5}. Since such splittings are not observed in the present case, we reject a C_{3v} symmetry, and assume that the molecule belongs to the C_{2v} point group. We can also exclude any change in the molecular symmetry on going from the liquid to the crystal, since both liquid and crystal spectra are virtually identical.

A second possibility is that the correlation diagram $C_{2v} \rightarrow C_2 \rightarrow C_{2h}$ derived from the crystallographic data, may be applied:



Even on this basis it is still not possible to explain the doublet structure of the bands. Each molecular vibration should give rise to only one infrared active component in the crystal. The third alternative is that the solid state spectrum may be interpreted in term of the correlation:



Each molecular vibration should now give rise, via dynamic coupling with the neighbouring molecules in the unit-cell, to two components, infrared active and polarized at 90° to one another. For bands which do not show any dichroism it may be assumed that the separation between the A' and A'' components is below the order of instrumental resolution*.

The correlation $C_{2v} \rightarrow C_1 \rightarrow C_s$ derives further support from the fact that Frenz *et al.*, on the basis of X-ray systematic absences, do not exclude the possibility of $C_s^4 - Cc$ space group.

Raman measurements, attempted with liquid samples, were unsuccessful because the compound decomposes under the action of the He-Ne laser beam. Furthermore, the impossibility of exactly locating the crystal face of crystalline films studied in infrared, did not allow the application of the oriented-gas model. In these circumstances a definite assignment of the fundamental modes of $Mn(CO)_4NO$ cannot be given.

* Very small separations, of the order $0.2\text{--}0.3\text{ cm}^{-1}$, between spectra in parallel and perpendicular light were found even in these cases.

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REFERENCES

- 1 P. M. Treichel, E. Pitcher, R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 83 (1961) 2593.
 - 2 B. A. Frenz, J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 8 (1969) 1288.
 - 3 H. Wawersik and F. Basolo, *J. Amer. Chem. Soc.*, 89 (1967) 4626.
 - 4 R. Cataliotti, A. Foffani and L. Marchetti, *Inorg. Chem.*, 10 (1971) 1594.
 - 5 R. Cataliotti, G. Paliani and A. Poletti, *Chem. Phys. Letters*, 11 (1971) 58.
 - 6 A. Poletti, R. Cataliotti and G. Paliani, *Spectrochim. Acta*, submitted.
 - 7 A. Poletti, R. Cataliotti and A. Foffani, *Inorg. Chim. Acta*, 2 (1968) 157.
 - 8 W. A. Seth-Paul, *J. Mol. Structure*, 3 (1969) 403.
 - 9 (a) *International Tables for X-Ray Crystallography*, Vol 1, Kynoch Press, Birmingham, 3rd ed., 1969; (b) R. S. Halford, *J. Chem. Phys.*, 14 (1946) 8.
- J. Organometal. Chem.*, 43 (1972)