

three-fold excess of D_2O to the compound, pumping off the heavy water and repeating the process a number of times.

N-methylthiopropionamide molecule belongs to the point group C_s . The fundamental frequencies which are classified as eleven in-plane (A') and four out of plane (A'') vibrations are active both in the infrared and the Raman spectra. While the bands at 3395 cm^{-1} and 3225 cm^{-1} are assigned to the free and the bonded N-H stretching vibrations, the corresponding mode of vibration of the N-D linkage gives rise to absorptions at 2450 cm^{-1} and 2385 cm^{-1} . The amide II and the amide III absorption bands in N-methylthiopropionamide which are at 1540 cm^{-1} and 1365 cm^{-1} are due to the combined contribution of the δ (N-H) and ν (C-N) vibrations while the corresponding peaks in its deuterated species are at 1500 cm^{-1} and 1220 cm^{-1} respectively. A comparison of the observations in Tables II and III would indicate that the N-H and N-D stretching frequencies in N-methylthiopropionamide are lower and the frequency of the amide III band is higher than those of the corresponding absorptions in N-methylpropionamide. This pattern of variation is similar to the one observed in cases of N-methylthioacetamide^{1,2} and N-methylacetamide⁴. On the other hand, the frequency of the amide II band is almost the same in both N-methylthiopropionamide and N-methylpropionamide. The band at 675 cm^{-1} is assigned to the C=S stretching vibration and this is the strongest band in the laser Raman Spectrum. While the N-H stretch, the amide III and the amide IV absorption bands show considerable variation in their frequencies on deuteration, the change in the frequency of the amide II band is only about 40 cm^{-1} .

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INFRARED SPECTRUM OF 1-FLUORO-2 : 4-DINITROBENZENE

1-FLUORO-2 : 4-Dinitrobenzene is a trisubstituted benzene wherein three hydrogen atoms of benzene ring are replaced by a fluorine atom and two NO_2 groups. A study of the infrared spectrum of this molecule in liquid phase was undertaken to obtain

detailed information about the fundamental vibrations in the ground state.

The infrared spectrum of 1-Fluoro-2 : 4-Dinitrobenzene, contained in a cell, has been recorded in liquid phase in the region $4000\text{--}250\text{ cm}^{-1}$ on a Perkin Elmer double beam Infrared Spectrophotometer. The thickness of the liquid cell was 0.025 mm . The sample was obtained from B.D.H. Company, England, and was used without further purification. 67 bands have been observed and analysed in terms of various ground state vibrations.

1-Fluoro-2 : 4-dinitrobenzene molecule belongs to C_s point group having the plane of the molecule as the only element of symmetry. In this case there are two types of probable vibrations, namely, a' and a'' . a' vibrations are totally symmetric and give rise to polarised Raman lines whereas a'' vibrations are anti-symmetric and give rise to depolarised Raman lines. The analysis of the bands and the assignment of the fundamental frequencies have been done on the basis of comparison with those of similar molecules as neither the polarisation of Raman lines nor the shape of the infrared bands in vapour phase is known. The infrared trace of the molecule in the liquid phase is reproduced in Fig. 1 and the wavenumbers of the bands along with their probable assignments are given in Table I.

C-H stretching frequencies.—There are six C-H stretching frequencies in benzene with the following modes of vibrations :

$3062 (a_{1g})$, $3060 (b_{1u})$, $3047 (e_{2g})$ and $3080 (e_{1u})$.

The last two frequencies are doubly degenerate. In the case of trisubstituted benzenes only three C-H stretching frequencies are expected as the other three frequencies would depend upon the mass and nature of the substituents. Out of these three frequencies only two frequencies at 3095 and 3110 cm^{-1} have been observed with very strong intensities and have been assigned to C-H stretching mode of vibration.

C-H bending modes.—The C-H bending modes in substituted benzenes occur in two different frequency regions $1000\text{--}1300\text{ cm}^{-1}$ (in-plane bending) and $750\text{--}1000\text{ cm}^{-1}$ (out-of-plane bending modes). The six C-H in-plane bending modes are derived from a_{2g} (1340), b_{2u} (1152), e_{2g} (1178) and e_{1u} (1037) modes of benzene in which e_{2g} (1178) and e_{1u} (1037) are doubly degenerate. In the present case two frequencies at 1125 and 1148 cm^{-1} have been assigned to C-H in-plane bending mode of vibration. This interpretation finds support from the infrared spectrum of 2-chloro-4-nitroaniline in

which 1117, 1150 and 1250 cm^{-1} vibrations have been assigned to C—H in-plane bending mode¹.

The six C—H out-of-plane bending vibrations in benzene arise from b_2 , (995), e_{2u} (975), e_1 , (850)

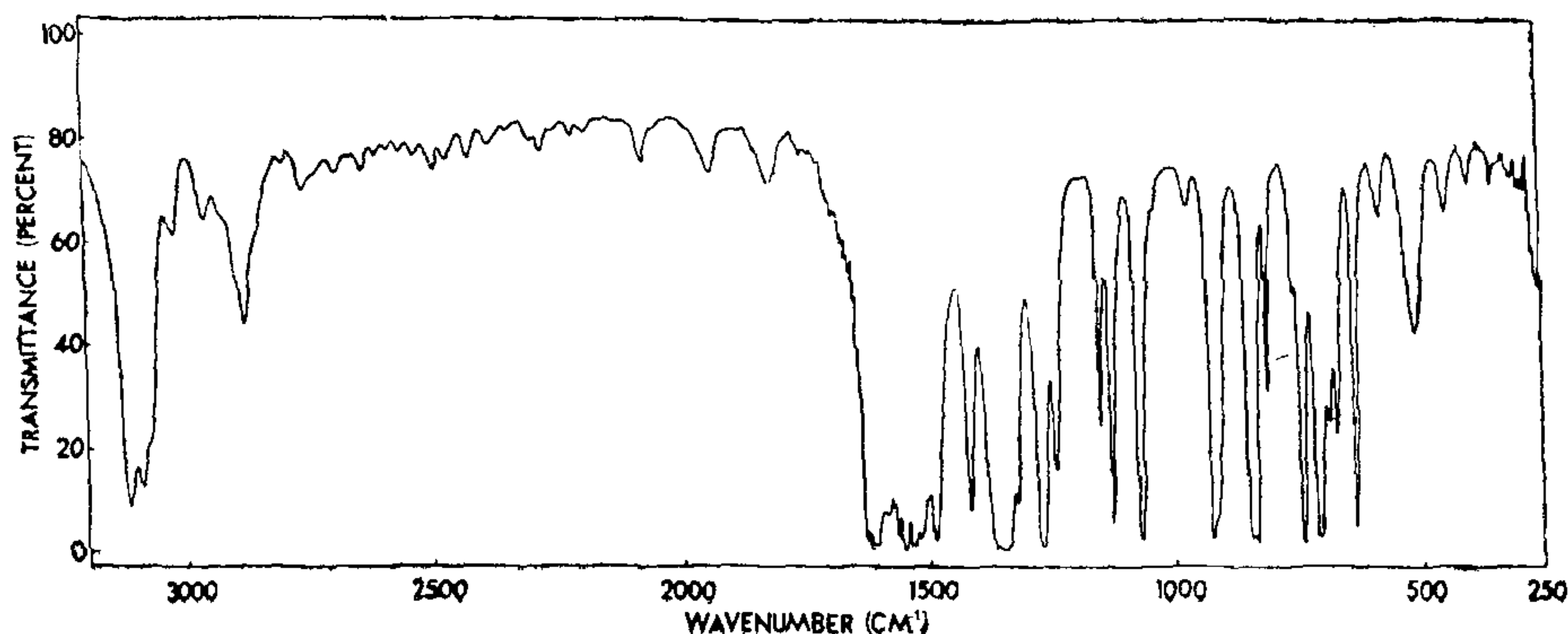


FIG. 1. I.R. spectrum of 1-fluoro-2,4-dinitrobenzene

TABLE I
Vibrational frequencies and assignments for 1-fluoro-2,4-dinitrobenzene

Infrared frequencies in cm^{-1}	Intensity	Assignment	Infrared frequencies in cm^{-1}	Intensity	Assignment
255	4	a' C—C bending o.p.	1455	shoulder	
265	3		1485	8, sharp	a' C—C stretching
270	2		1490	7, sharp	A'' 735 + 755
290	1		1505	shoulder	A' 2 × 755
305	2, sharp		1515	9	A'' 809 + 705
345	2, do.		1530	9	
395	2, do.		1535	8	A'' 835 + 705
445	3, do.	a'' NO ₂ rocking	1545	8	A'' 809 + 735
505	5, do.	a' C—C—C ring deformation i.p.	1555	9	a'' NO ₂ asymmetric stretching
575	3, do.		1565	9	A'' 1125 + 445
630	8, very sharp	a' C—C—C ring deformation i.p.	1575	9	A' 1065 + 505
665	5, do.		1585	shoulder	A' 835 + 755
685	5, sharp		1610	9, broad	a' C—C stretching
705	8, very sharp	a' C—F bending i.p.	1620	8, sharp	a' do.
735	9, do.	a' Ring breathing	1625	shoulder	A' 1125 + 505
755	4, sharp	a'' C—H bending o.p.	1650	4	
809	6, very sharp	a'' do.	1655	3	A' 1148 + 505
835	9, do.	a'' do.	1665	2	
845	9		1670	2	A'' 1415 + 255
915	shoulder		1675	2	A'' 1235 + 445
920	9, very sharp	a' C—NO ₂ stretching	1685	2	
985	2	A' 705 + 255	1815	2, broad	A' 1555 + 255
1035	shoulder		1935	2, do.	A'' 1485 + 445
1065	9, very sharp	a' C—C—C trigonal bending	2075	2, do.	A'' 1620 + 445
1125	8, do.	a' C—H bending i.p.	2710	2	A' 1365 + 1350
1148	6, do.	a' do.	2890	1	A'' 1485 + 1320
1235	7, do.	a' C—F stretching	2925	shoulder	A'' 1555 + 1365
1270	9, broad	A_8 2 × 630	2960	2	A' 2 × 1485
1320	8, sharp	a' C—N stretching	3025	2	
1335	shoulder	A' 705 + 630	3098	7, sharp	a' C—H stretching
1350	9, broad	a' C—C stretching	3110	8, do.	a' do.
1365	9	a' NO ₂ symmetric stretching	3235	1	A' 2 × 1620
1415	8, very sharp	a' C—C stretching	3620	2	A' 3110 + 505
			3630	2	

Note: Visual estimates of the intensities have been taken on the scale 0 to 10, i.p. = in-plane, o.p. = out-of-plane.

and a_{2u} (637) modes. In trisubstituted benzenes only three C—H out-of-plane bending vibrations are observed and the remaining three vibrations correspond to bending modes of the substituents. In the present case three bands at 755, 809 and 835 cm^{-1} have been assigned to C—H out-of-plane bending mode. Similar assignments have been made in 2-chloro 4-nitroaniline¹ for the frequencies 760 and 815 cm^{-1} .

C—F stretching mode.—The infrared spectra of a number of mono and disubstituted fluorine derivatives have been studied by Narasimham *et al.*² and those of tri and tetra-fluoro benzenes by Ferguson *et al.*³. They have assigned the frequency 1250 cm^{-1} to C—F stretching vibration. In analogy to these assignments the strong band at 1235 cm^{-1} in 1-fluoro-2 : 4-dinitrobenzene has been assigned to C—F stretching mode of vibration. Magnitudes of this frequency in some fluorinated benzenes are given in Table II.

TABLE II

Molecule	C—F stretching vibration in cm^{-1}
<i>m</i> -Difluorobenzene ⁴	1288
<i>p</i> -Difluorobenzene ⁵	1259
<i>m</i> -Fluorotoluene ⁶	1275
<i>o</i> -Fluorochlorobenzene ⁷	1248
<i>m</i> -Fluorochlorobenzene ⁷	1229
<i>p</i> -Fluorochlorobenzene ⁷	1239

Vibrations of C—NO₂ group.—NO₂ symmetric and asymmetric stretching frequencies have been assigned at 1365 and 1555 cm^{-1} respectively in the present case. This assignment is in agreement with following assignments made in different molecules.

Molecule	NO ₂ symmetric stretching frequency in cm^{-1}	NO ₂ asymmetric stretching frequency in cm^{-1}
<i>o</i> -Nitrophenetole ⁸	1354	1515
<i>p</i> -Nitrophenetole ⁸	1344	1516
2-Chloro-4-nitroaniline ¹	1367	1550
4-Chloro-2-nitroaniline ¹	1350	1530

All other bands have been assigned as some fundamentals and combinations of fundamental frequencies.

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CYANATO COMPLEXES OF MANGANESE (II) WITH NITROGEN DONOR LIGANDS

SEVERAL cyanato complexes in which NCO group functions either as a monodentate being bonded through nitrogen¹⁻⁶ or as a bidentate being bonded through N-atom bridging^{1,7} or —NCO-bridging have been reported earlier. This communication describes the results of our studies on some cyanato complexes of manganese(II) with pyridine, β -picoline, 3, 5-lutidine, 3-ethyl pyridine, 3-bromopyridine and isoquinoline.

All the chemicals used were A.R. grade. The complexes were prepared by reacting an aqueous solution of hydrated manganous nitrate with an aqueous solution of potassium cyanate in the ratio 1 : 2 and then adding calculated amount of the ligands as described earlier¹. The composition of the isolated compounds was established by estimating the metal by standard method. The conductance measurements were carried out in dimethyl-formamide using a Toshniwal conductivity bridge and magnetic susceptibilities were determined for solid specimens using the Gouy method. Infra-red spectra were recorded using a Unicam SP-200 spectrophotometer with specimens mounted in Nujol. Relevant analytical, melting point, conductance, magnetic susceptibility and infra-red spectral data are recorded in Table I.

More frequently, divalent manganese ion forms six-coordinated, octahedral complexes involving the use of $4s^4 p^3 d^2$ bonding orbitals. The complexes reported now have the composition $\text{MnL}_4(\text{NCO})_2$ where L is a nitrogen donor ligand. They are all paramagnetic and μ_{eff} values ranging between 5.56 and 6.01 B.M. indicate the presence of five unpaired electrons. The complexes are soluble in demethylformamide in which medium electrical conductance was measured. The molar conductance values, Λ_m , of 6 to 12 mhos (Table I) are