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K. Chhor [a] , C. Pommier [a] & M. Diot [b]
[a] Laboratoire de Chimie-Physique, C.S.P., Université PARIS-NORD, Avenue J. B. Clément, 93430 Villetaneuse (France), E.R.A. CNRS N° 456
[b] Laboratoire de Physico-Chimie Minérale de l'Institut National des Sciences Appliquées de Lyon, Avenue Albert-Einstein, 69621 Villeurbanne (France), E.R.A. CNRS N° 116
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K. CHHOR and C. POMMIER

Laboratoire de Chimie-Physique, C.S.P., Université PARIS-NORD, Avenue J. B. Clément, 93430 Villetaneuse (France), E.R.A. CNRS N° 456

and

M. DIOT

Laboratoire de Physico-Chimie Minérale de l'Institut National des Sciences Appliquées de Lyon, Avenue Albert-Einstein, 69621 Villeurbanne (France), E.R.A. CNRS N° 116

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The heat capacities of the complexes $C_5H_5Mn(CO)_3$ and $C_4H_4NMn(CO)_3$ were measured from 10 to 300 K by an adiabatic calorimeter and the thermodynamic functions reported. For $C_5H_5Mn(CO)_3$ the heat capacity appears to be to some degree "abnormally" high in the temperature range 75–135 K. This small anomaly is discussed in connection with our vibrational results. For $C_4H_4NMn(CO)_3$, there is no anomaly of the Cp curve between 10 and 300 K, however a phase transition is detected by DTA at 315.5 K, (about 10 K below the melting point) associated with an enthalpy variation $\Delta H = 1910 \pm 40$ J mol^{-1}. An attempt is made to calculate the "normal" Cp curves from spectroscopic data and to estimate the compressibility for both compounds. Finally, we compare the thermal behaviour of these compounds with those of other arene metal carbonyls in terms of disorder and lattice energy.

I. INTRODUCTION

The thermal behaviour and the molecular dynamics of transition metal π complexes (metallocenes and arene metal carbonyls) have been studied by calorimetric and spectroscopic methods (IR, Raman scattering and quasielastic neutron scattering).[1–19] From Raman and

neutron scattering experiments we have shown previously that the aromatic rings are able to undergo jumps in the solid state and the associated potential barrier ranges between 4 and 16 kJ mol^{-1}.[1-9] This freedom of ring reorientation in these crystals leads to many equilibrium positions. If these allowed orientations are distinguishable, when the temperature is raised, a phase transition can occur from an ordered phase into a disordered one. These situations have been observed particularly in ferrocene, nickelocene,[2,15] thiophene chromium tricarbonyl,[3,4,16] phospholyl manganese tricarbonyl.[11]

The C_5H_5 ring in cymantrene $C_5H_5Mn(CO)_3$ (referred to hereafter as CpMnT) has been recently studied by incoherent quasielastic neutron scattering.[9] In this case the activation energy (16.8 kJ mol^{-1}) and the correlation time ($\tau_c = 1.7\ 10^{-11}$ s) are somewhat different from those deduced from spin lattice relaxation time T_1 in NMR experiments: $E_a = 7.2$ kJ mol^{-1} and $\tau_c = 6.4\ 10^{-13}$ s.[20]

Crystallographic study on CpMnT at room temperature has shown that this compound crystallizes in a monoclinic system with four molecules per unit cell, located on sites of C_1 symmetry.[21] Its structure has been redetermined recently[22] and the distortion of the C_5H_5 ring has been emphasized. The same conclusion was obtained from spectroscopic studies.[23-27]

The existence of a phase transition taking place between 77 and 300 K has been controversial. From vibrational studies down to 80 K, Hyams *et al.*[27] reported that a low temperature phase transition could occur. However Adams *et al.*[23] disproved this eventuality and explained the appearance of many bands on the low temperature spectra by degeneracy removal and unit cell multiplicity. Recently Berar *et al.* found no anomaly in the evolution of the cell parameters and the thermal expansion coefficient between 80 and 300 K.[28]

Azacymantrene $C_4H_4NMn(CO)_3$ (referred to hereafter as PyMnT) is isomorphous with cymantrene at 300 K.[29] The vibrational study of this complex has been reported by Lokshin *et al.*[30] at room temperature. However, there is no structural study below 300 K.

In a recent paper we have evidenced an order-disorder phase transition in phospholyl manganese tricarbonyl $C_4H_4PMn(CO)_3$ (monoclinic-triclinic, $T_t = 115$ K) from heat capacity measurements, X-Ray diffraction and low frequency Raman scattering.[11] In the present work we report the heat capacities of CpMnT and PyMnT from 10 to 300 K. Their thermal behaviour will be discussed in relation to spectroscopic results and compared with those of other arene metal carbonyls.

II. EXPERIMENTAL

Samples. The studied CpMnT is a commercial product (Alfa Inorganic, Germany) purified by repeated recrystallizations in hexane. The purity of the sample has been controlled by IR, RMN spectroscopies and chemical analysis:

$$C\%\begin{cases}47.17\ (\text{found.})\\47.00\ (\text{theor.})\end{cases}\qquad H\%\begin{cases}2.44\ (\text{found.})\\2.45\ (\text{theor.})\end{cases}\qquad Mn\%\begin{cases}27.00\ (\text{found.})\\27.00\ (\text{theor.})\end{cases}$$

The PyMnT was prepared from $Mn_2(CO)_{10}$ and pyrrole in octane according to the method described by Pauson *et al.*.[31] The crude product was purified by chromatography, and recrystallizations in hexane. Chemical analysis shows the following composition:

$$C\%\begin{cases}41.15\ (\text{found.})\\41.58\ (\text{theor.})\end{cases}\qquad H\%\begin{cases}1.94\ (\text{found.})\\1.98\ (\text{theor.})\end{cases}$$

$$N\%\begin{cases}6.66\ (\text{found.})\\6.93\ (\text{theor.})\end{cases}\qquad Mn\%\begin{cases}27.28\ (\text{found.})\\25.75\ (\text{theor.})\end{cases}$$

Apparatus. The thermal analysis was performed either on a differential scanning calorimeter (M.C.B. Arion Grenoble, France) (the heating and the cooling rates are 0.5 K min^{-1} and the sample weight is about 300 mg) or on a Mettler TA 2000 calorimeter (Zurich, Switzerland) (the heating and the cooling rates range between 1 and 5 K min^{-1} and the sample weight is about 20 mg).

The heat capacity measurements were performed on an adiabatic calorimeter described in ref. 39. A gold-plate copper calorimeter with an internal volume of 20 cm^3 was used. When the calorimeter was loaded with the sample, helium gas was added (15 kPa at 300 K) to enhance the thermal contact between calorimeter and sample. It was sealed, placed in the cryostat and cooled.

The heat capacity of the empty calorimeter was determined in a separate experiment using the same amounts of indium joint and apiezon-N grease. The heat capacity of the sample represented 25 to 60 per cent of the total heat capacity. The estimated error is about 15% under 15 K, 2% from 15 to 40 K and decreases down to 0.5% around 250 K.

For experiments on PyMnT, the sample amount used is two times smaller than for CpMnT, and the estimated error increases in the same proportion.

TABLE I

Experimental values of the heat capacity of $C_5H_5Mn(CO)_3$

$\frac{T}{K}$	Cp / $JK^{-1}mol^{-1}$	$\frac{T}{K}$	Cp / $JK^{-1}mol^{-1}$	$\frac{T}{K}$	Cp / $JK^{-1}mol^{-1}$	$\frac{T}{K}$	Cp / $JK^{-1}mol^{-1}$
Series 1		Series 5		Series 8		Series 10	
269.64	201.05	84.01	86.19	228.72	174.08	72.20	79.94
272.75	202.90	88.14	87.84	233.53	177.50	75.27	81.49
276.12	204.00	92.14	89.35	238.69	180.44	78.24	83.18
279.22	206.24	96.01	92.29	243.65	183.70	81.11	84.61
285.44	209.01	100.06	94.86	248.91	187.20	86.62	87.09
288.87	210.40	105.72	98.40	254.24	190.86	88.98	88.46
Series 2		109.78	101.00	259.55	193.09	91.28	89.00
199.11	154.74	113.73	103.02	264.52	197.04	Series 11	
202.93	158.55	117.89	105.92	269.44	200.10	54.70	67.80
206.76	160.48	122.22	106.52	274.15	203.08	57.83	70.77
210.66	162.05	125.45	109.79	278.20	204.02	61.07	73.12
214.62	165.35	130.64	111.78	282.13	207.34	64.13	75.73
218.56	168.58	134.73	114.06	286.25	210.83	67.05	77.68
222.41	171.01	138.76	116.60	290.25	212.09	69.87	79.30
226.14	173.97	142.76	119.21	Series 9		72.59	80.46
229.98	176.19	146.60	121.41	6.948	1.845	75.23	81.87
233.70	177.06	150.42	123.86	9.313	4.070	77.80	83.14
237.31	179.12	157.96	128.18	11.85	7.198	80.29	84.50
Series 3		Series 6		13.44	10.04	82.72	86.43
231.41	177.05	157.23	128.00	15.85	13.03	85.09	87.17
235.16	178.07	161.00	131.26	18.22	17.75	87.61	88.58
238.87	181.30	164.82	133.42	20.49	21.00	90.27	88.43
242.42	183.46	168.59	134.94	22.23	23.08	92.87	89.90
246.31	184.83	172.26	138.10	23.96	27.07	95.42	91.49
250.46	187.73	175.90	140.03	25.54	29.90	Series 12	
254.39	189.86	179.46	143.37	29.53	36.61	104.50	97.88
258.37	192.67	182.95	145.09	32.79	41.94	107.20	99.33
262.12	196.68	186.02	146.87	36.37	47.15	109.89	101.32
265.80	197.83	189.42	148.43	38.43	50.06	112.56	102.34
Series 4		Series 7		40.19	52.42	115.24	104.06
79.86	84.55	223.12	171.04	43.90	57.31	117.94	105.51
84.22	86.10	227.81	173.08	47.58	60.87	120.68	106.90
88.23	88.12	232.32	177.02	51.23	64.49	123.48	108.27
97.27	89.87	236.78	179.42	54.89	67.86		
96.13	92.17	241.07	182.05	58.54	70.90		
99.88	94.23			62.23	74.27		
103.51	97.22						
107.05	99.42						
110.51	100.93						
113.89	103.45						
117.20	104.52						

III. RESULTS

Cyclopentadienyl manganese tricarbonyl. DTA curves were recorded between 100 and 360 K with various cooling and heating rates. The only phenomenon encountered in this range is the melting of the crystals at 350 K associated with an enthalpy change $\Delta H = 19300 \pm 400$ J.mol^{-1}. The possible metastability of the room temperature

TABLE II

Thermodynamic functions of $C_5H_5Mn(CO)_3$

$\frac{T}{K}$	$\frac{Cp}{JK^{-1}\,mol^{-1}}$	$\frac{S°(T) - S°(0)}{JK^{-1}\,mol^{-1}}$	$\frac{H°(T) - H°(0)}{J\,mol^{-1}}$	$\frac{-\{G°(T) - H°(0)\}/T}{JK^{-1}\,mol^{-1}}$
5	0.726	0.250	0.940	0.062
10	4.850	1.785	13.17	0.468
15	12.20	5.076	54.99	1.410
20	20.09	9.676	135.9	2.882
25	28.71	15.07	257.5	4.767
30	37.34	21.07	422.8	6.977
35	45.26	27.43	629.7	9.442
40	52.24	33.94	873.9	12.10
45	58.25	40.45	1150	14.89
50	63.39	46.86	1454	17.76
60	72.47	59.24	2135	23.65
70	79.14	70.91	2894	29.56
80	84.30	81.84	3713	35.43
90	88.83	92.02	4578	41.16
100	94.58	101.7	5494	46.73
110	101.07	111.0	6472	52.15
120	106.39	120.0	7510	57.44
130	111.52	128.7	8599	62.59
140	117.46	138.1	9856	67.67
150	123.58	146.4	11061	72.64
160	129.89	154.5	12328	77.51
170	136.37	161.7	13548	82.08
180	142.96	169.8	14944	86.73
190	149.58	177.7	16407	91.31
200	156.15	185.5	17936	95.83
210	162.61	193.3	19529	100.28
220	168.98	201.0	21188	104.68
230	175.26	208.6	22909	109.04
240	181.54	216.2	24694	113.34
250	187.84	223.8	26540	117.61
260	194.79	231.3	28450	121.83
270	200.43	238.7	30424	126.03
273.15	202.36	241.1	31058	127.34
280	206.40	246.1	32458	130.18
290	211.63	253.4	34549	134.31
298.15	214.79	259.35	36289	137.64
300	215.32	260.7	36689	138.39

phase at low temperature has been checked: no modification of the DTA curves is observed when the sample is annealed 2 days at 100 K before heating.

The experimental values of the molar heat capacities are reported in Table I. They appear in chronological order and are corrected for curvature. The values of Cp, $S°(T) - S°(0)$, $H°(T) - H°(0)$ and $-\{G°(T) - H°(0)\}1/T$ are listed at selected temperatures in Table II. These values were obtained by a least square fit to the experimental points. Values below 8 K were extrapolated with a Debye T^3 heat capacity function. The probable error of the thermodynamic functions due to the fitting is less than 1%. An additional digit beyond those significant is given to permit interpolation and differentiation.

Pyrrolyl manganese tricarbonyl. Figure 1 summarizes the thermograms obtained on PyMnT between 100 and 350 K. On heating, a small endothermic peak is observed at 305 K just before the melting point at 315.5 K. On cooling both phenomena show an important hysterisis effect of about 26 K. However the enthalpies associated with these transitions do not depend on the thermal history of the sample:

	Solid–Solid phase transition	Fusion
Temperature (K)	305	315.5
ΔH(J mol^{-1})	1910 ± 40	13010 ± 260

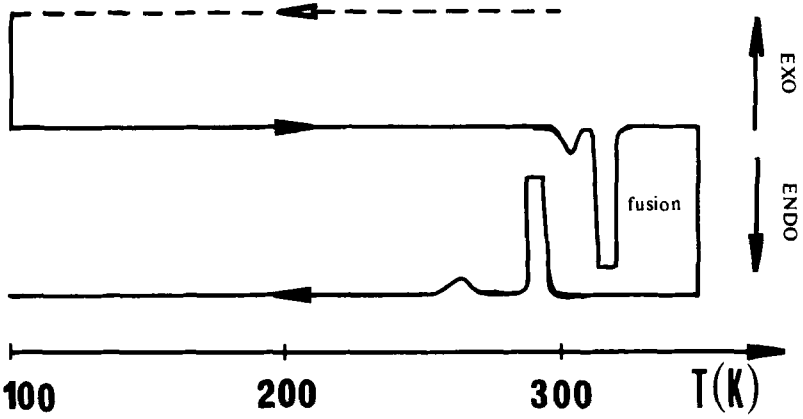

FIGURE 1 DTA curves of $C_4H_4NMn(CO)_3$ between 100 and 350 K.

TABLE III

Experimental values of the molar heat capacity of $C_4H_4NMn(CO)_3$

$\frac{T}{K}$	$\frac{Cp}{JK^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{Cp}{JK^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{Cp}{JK^{-1}\,mol^{-1}}$
Series 1		Series 3		Series 6	
87.45	88.22	253.77	189.15	9.61	0.288
91.55	90.27	258.22	191.06	10.06	0.504
95.38	92.43	262.42	194.40	12.00	1.66
98.87	95.12	266.56	196.74	13.63	5.84
102.36	97.76	270.44	198.52	14.95	9.25
105.56	99.56	274.30	201.65	16.62	3.98
108.63	101.24	277.88	203.61	18.42	1.71
111.81	103.17	281.48	206.93	19.92	15.85
115.28	104.64	284.75	207.91	20.87	16.21
119.80	107.29	288.10	211.30	21.75	17.85
125.09	110.29	Series 4		22.94	18.08
130.24	112.83	11.20	0.902	25.04	22.71
135.30	116.06	12.37	2.10	27.16	28.20
140.23	119.94	14.31	7.73	28.91	33.22
145.07	122.95	15.82	5.65	30.46	34.65
149.81	125.72	17.73	2.09	32.14	37.27
158.99	130.99	19.55	9.12	33.92	42.57
163.47	133.47	20.92	15.97	36.75	46.28
167.84	136.51	22.45	18.40	40.13	51.97
172.11	138.69	Series 5		43.35	56.32
176.31	141.44	10.62	0.740	46.83	60.43
180.40	144.22	11.41	1.23	51.00	64.38
184.42	147.07	12.54	3.03	55.54	68.63
188.36	148.34	13.22	4.55	59.67	71.54
192.20	150.57	14.22	6.98	63.48	73.97
195.96	151.18	14.98	9.18	67.05	76.27
199.62	154.51	15.89	5.53	70.43	78.13
Series 2		16.64	6.01	73.67	80.57
207.56	159.34	17.64	1.97	76.78	82.31
213.15	162.68	18.76	1.88	79.78	84.15
218.60	166.41	19.97	10.03	83.03	26.27
223.97	169.46	21.02	16.45	86.53	88.25
234.25	176.40	22.46	18.26		
239.20	180.45	23.97	20.75		
243.96	182.55	25.26	23.75		
248.61	185.40	26.52	26.18		
253.04	188.49	27.99	29.49		
257.49	193.00				
261.68	194.98				
265.85	196.30				
269.75	200.14				

TABLE IV

Thermodynamic functions of $C_4H_4NMn(CO)_3$

T / K	Cp / $JK^{-1}\,mol^{-1}$	$S°(T) - S°(0)$ / $JK^{-1}\,mol^{-1}$	$H°(T) - H°(0)$ / $J\,mol^{-1}$	$-\{G°(T) - H°(0)\}/T$ / $JK^{-1}\,mol^{-1}$
20	9.54	3.71	36.6	1.880
25	22.96	7.32	118.8	2.571
30	34.26	12.54	262.7	3.782
35	43.69	18.55	458.3	5.456
40	51.54	24.91	696.9	7.488
45	58.05	31.27	971.5	9.783
50	63.47	37.78	1275.7	12.26
60	71.88	50.13	1954.6	17.56
70	78.33	61.71	2706.7	23.05
80	84.03	72.55	3518.7	28.56
90	89.72	82.77	4387.2	34.02
100	95.64	92.53	5313.9	39.39
110	101.6	101.9	6300.4	44.65
120	107.7	111.0	7347.0	49.80
130	113.7	119.9	8453.9	54.86
140	119.7	128.5	9620.6	59.81
150	125.6	137.0	10847	64.68
160	131.5	145.3	12132	69.45
170	137.4	153.4	13477	74.16
180	143.3	161.4	14880	78.78
190	149.2	169.4	16342	83.34
200	155.2	177.2	17864	87.84
210	161.2	184.9	19446	92.28
220	167.4	192.5	21089	96.66
230	173.7	200.1	22795	99.11
240	180.0	207.6	24563	105.28
250	186.4	215.1	26395	105.58
260	192.9	222.5	28292	113.73
270	199.3	229.9	30252	117.89
273.15	201.3	232.3	30884	119.20
280	205.6	237.3	32277	122.03
290	211.6	244.6	34363	126.13
298.15	216.2	250.5	36106	129.45
300	217.2	251.9	36507	130.20

The experimental values of molar heat capacities are reported in chronological order in Table III. The fitted Cp values and the calculated thermodynamic functions are reported in Table IV.

Anomalous Cp values are observed between 15 and 20 K on three different series. Nevertheless, actually no explanation is proposed for this phenomenon occurring in a region where the transitions are generally magnetic in nature.[19]

IV. DISCUSSION

IV-1. Comparison between the experimental and spectroscopic values of the heat capacity

Cyclopentadienyl manganese tricarbonyl. The Cp experimental values are displayed in Figure 2. No major anomaly is observed, however from about 75 to 135 K the heat capacity is higher by about 1% than might be expected from the general trend of the curve. In order to be precise about this point we compare the experimental values with the calculated one from spectroscopic data.

We shall assume that the heat capacity can be written as the sum of three terms.

$$C_p = (C_p - C_v) + C_v^l + C_v^{\text{int}} \tag{1}$$

C_v^l and C_v^{int} are the contributions from the lattice and the internal vibrations, respectively. The evaluation of $(C_p - C_v)$ is based on the thermodynamic relation

$$C_p - C_v = \alpha^2 VT/\beta \tag{2}$$

where α is the thermal expansion coefficient, V is the molar volume and β is the compressibility. In the absence of an experimental β value, recourse is made to the Lord's expression[32]

$$C_p - C_v = AC_p^2 T \tag{3}$$

The lattice vibration contribution is calculated from a six fold Debye function with a Debye temperature estimated from the experimental result at 25 K: $\theta_D = 105$ K (corresponding to a cut off frequency $\nu_D = 73\ \text{cm}^{-1}$).

In order to calculate C_v^{int} we have reinvestigated the Raman spectra especially in the low frequency range[7] where the assignments proposed previously in the literature are open to criticism.[23-27] The contribution of these internal modes to the heat capacity was estimated using Einstein functions. The variation of internal frequencies between 5 and 300 K is found sufficiently small to be neglected in the calculation of C_v^{int} (the error is less than 0.1% at 100 K).

The value of the parameter A in eq. (3) has been determined from the experimental heat capacities in the temperature range where the

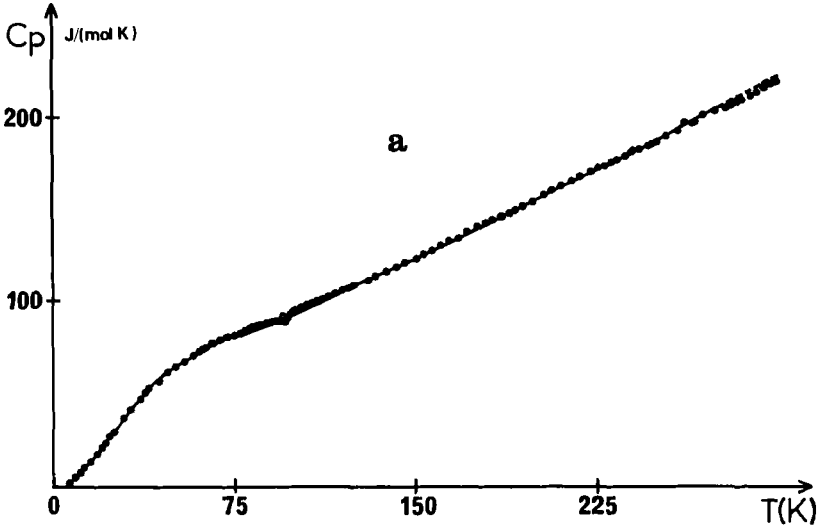

FIGURE 2 Molar heat capacity Cp of $C_5H_5Mn(CO)_3$ against temperature, plotted from a representative selection of the experimental results. The full line corresponds to the calculated Cp curve.

Cp curve appears as "normal" ($T > 150$ K): $A = 2.10^{-6}$ J^{-1} mol.; $(C_p - C_v)$ is then about 3% of Cp value at 150 K and increases to about 11% at 300 K.

X-Ray measurements allow the determination of the molar volume V and the thermal expansion coefficient α_v from 80 to 280 K.[28] The compressibility β can be deduced from eqs. (2) and (3): at 280 K, $\beta = 0.5\ 10^{-5}$ cm^2/kg. This value is consistent with those reported for various molecular crystals by Bridgman.[33]

The calculated curve is reported on Figure 2. The experimental and calculated values are in agreement below 70 K and above 150 K within $\pm 0.5\%$. However, in the temperature range 75–135 K a slight discrepancy is revealed. The experimental values are 1 to 2% higher than the calculated ones. To establish the reality of this effect, more than 50 experimental measurements have been made in this range corresponding to four different series (Table I, Figure 2b).

Pyrrolyl manganese tricarbonyl. The molar heat capacity curve of PyMnT between 20 and 300 K is given on Figure 3. As mentioned above, no anomaly is observed. As for CpMnT, the calculated heat capacities can be obtained from spectroscopic results. The Debye temperature calculated at 30 K is $\theta_D = 112$ K, which corresponds to a cut off frequency, $\nu_D = 78$ cm^{-1}. In order to determine the C_v^{int} term

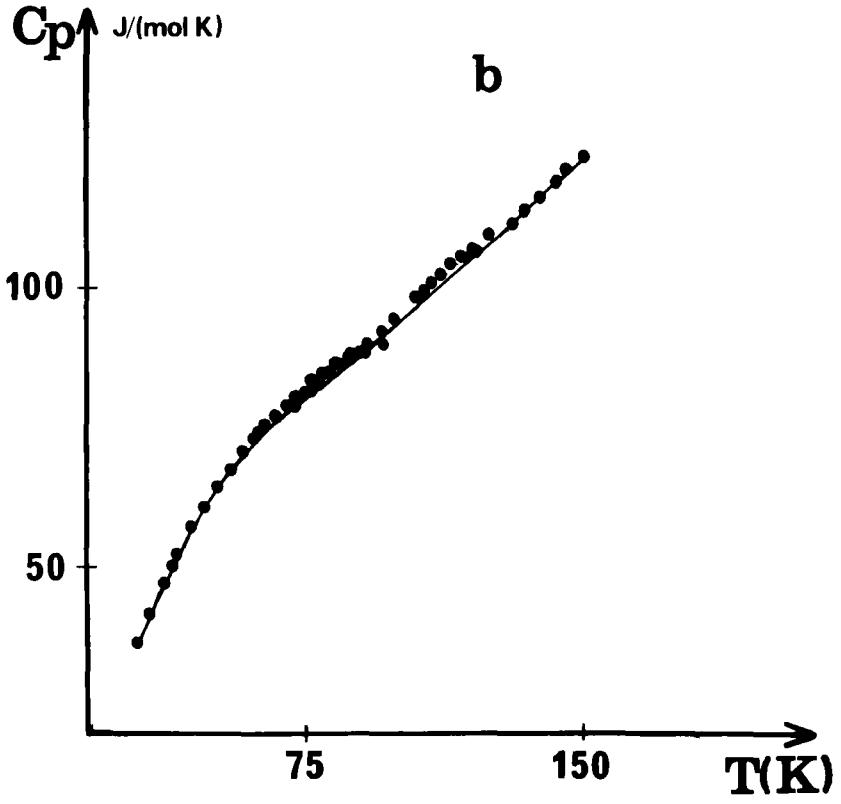

FIGURE 2 *Continued*

the low frequency internal modes ($\nu < 200$ cm^{-1}) have been assigned from the Raman spectra.[34] The A parameter in relation (3) is found to be equal to 2.85 10^{-6} J^{-1} mol.; ($C_p - C_v$) is about 4% of the Cp value at 150 K and increases to 14% at 300 K.

The agreement between the calculated and the experimental heat capacities over the whole temperature range is quite satisfactory as shown on Figure 3.

IV-2. Interpretation of thermal behaviour

Cyclopentadienyl manganese tricarbonyl. As mentioned above, the variation of entropy associated with the anomaly of the heat capacity curve, around 100 K, is very small and is estimated to be about 0.1% of the ΔS of the crystal at this temperature. This anomaly can be related to different causes, among which the presence of an impurity

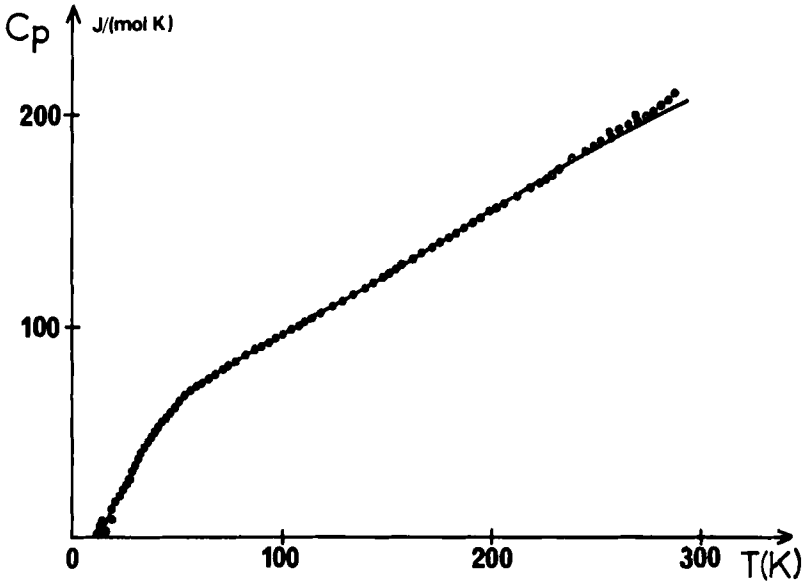

FIGURE 3 (●) Experimental heat capacity of $C_4H_4NMn(CO)_3$. (−) The full line indicates the heat capacity calculated as described in the text.

in the sample is not excluded. The purity obtained from chemical analysis is about 99%. Nevertheless a jump of Cp of 1% implies a change of 100% for the heat capacity of the impurity and insofar as the observed anomaly is broad, this hypothesis cannot be retained.

Another possibility to explain this effect is to consider that a diffuse order-disorder phase transition occurs around 100 K and the entropy variation ΔS is configurational in nature. Under this condition, the reorientational process of the molecule must lead to distinguishable configurations. Recently, we have performed quasielastic neutron scattering experiments on CpMnT and the broadening of the quasi-elastic peak observed in the temperature range 260–300 K can be interpreted in terms of a dynamical disorder induced either by $2\pi/5$ rotational jump of the C_5H_5 ring around the principal molecular axis, or by $2\pi/5$ jump of the molecule as a whole. The first assumption does not lead to any entropy increment in the crystal, the latter one gives rise to three distinguishable molecular configurations. The experimental value of the entropy change ($\Delta S < 1$ JK^{-1} mol^{-1}) is too weak to be accounted for a disorder (even a partial one) between three distinct molecular states.

In addition, we have shown from calorimetric and Raman studies on benzene chromium carbonyl complexes e.g. $C_6H_6Cr(CO)_3$,

$C_6H_6Cr(CO)_2CS$[3,5] that, in the solid state, below 350 K, the aromatic rings are able to execute jump motions, but the reorientation of the carbonyl groups are very improbable.

Consequently, on the basis of the neutron scattering results, we can consider that only $2\pi/5$ jumps of the C_5H_5 ring alone take place in the temperature range below 300 K, and the weak anomaly of the heat capacity, around 100 K, can be explained in terms of the transition from a small to a large amplitude motion of the C_5H_5 ring. From our Raman study,[7] the potential function curve associated with the C_5H_5 ring reorientation is slightly asymmetric, insofar as it results from the combination of two terms: the potential function governing the intermolecular motion of C_5H_5 ring which is of five fold order and the intramolecular potential function with a period of $2\pi/15$. Under this condition, one can consider that, at a given temperature e.g. 100 K, an important proportion of the aromatic rings execute large amplitude oscillation around the average equilibrium positions slightly displaced from those of the C_5H_5 rings oscillating with a small amplitude ($T < 70$ K).[7,14]

On the contrary for $C_6H_6Cr(CO)_3$, the potential curve associated with C_6H_6 ring reorientation is symmetric and the average equilibrium positions of the aromatic ring in the small and large amplitude oscillatory states are identical, consequently, no anomaly of the Cp has been observed between 10 and 300 K for this compound.[5,14]

Pyrrolyl manganese tricarbonyl. At 300 K, as for CpMnT, the PyMnT crystallizes in a monoclinic system, but the structure between 305 K and the melting point is unknown. However, some reasonable assumptions can be made to explain the thermal behaviour of this compound between 20 and 315 K particularly the transition at 305 K.

i) A first assumption would be to consider the transition at 315 K as order-disorder in nature, induced by the reorientational motion of the aromatic ring in the crystal, as for other compounds we have studied: e.g. $C_4H_4SCr(CO)_3$, $C_4H_4PMn(CO)_3$.[3,11,16] In this case, the $2\pi/3$ or $2\pi/5$ C_4H_4N ring jump around the molecular axis generates distinguishable molecular configurations. Assuming a total disorder in the high temperature phase, the transition from a complete ordered phase below 305 K must increase the entropy value by R Log 3 or R Log 5 respectively. The weaker experimental value of $\Delta S(\sim R \text{ Log } 2)$ could be explained by the fact that among the allowed molecular configurations in the disordered phase some have a very low population. However, these hypothesis appear to be unlikely: first, in the compounds with similar structure e.g. $C_5H_5Mn(CO)_3$,[7,9] $C_4H_4PMn(CO)_3$,[11] the onset of ring reorientational motion takes

place at much lower temperatures; secondly, it is difficult to justify that the distinct molecular configurations in the disordered phase could have noticeably different energies at 305 K.

ii) Another alternative is to consider that $C_4H_4NMn(CO)_3$ is substantially disordered at 300 K as for $C_4H_4PMn(CO)_3$[11] assuming that an order-disorder phase transition occurs below this temperature. As no anomaly is detected neither by DTA nor on the Cp curve, this transition is supposed to be associated with a weak enthalpy change and to occur over a large temperature range. Effectively the difference of energy between the ordered and the disordered states of the crystal must be weak, insofar as the random distribution of the nitrogen atoms on the distinct sites does not induce an important increase of the unit cell volume (the nitrogen Van der Waals radii is somewhat smaller than that of C-H group). Furthermore, in our preliminary isothermal Cp experiments performed on a differential scanning calorimeter according to the method described by Barberi *et al.*,[42] a broad anomaly has been detected between 150 and 240 K[35] (the maximum deviation is about 4% around 200 K). This method, as adiabatic calorimeter, allows measurements at thermal equilibrium states of the sample. It needs calibration with standards of similar thermal conductivity and so, the accuracy on the absolute Cp values is estimated to about 5%. However, the reproducibility of the measurements is better than 3%. From adiabatic experiments, because of the too low amount of the available sample (see § II), it is difficult to draw a conclusion about the existence of a diffuse phase transition below 300 K. Finally, our low frequency Raman studies on $C_4H_4NMn(CO)_3$ have shown that the spectra at 300 K exhibit broad lines in agreement with the existence of a disordered structure of the crystal.[34]

Then, the phase transition observed at 305 K (about 10 K below the melting point) could be tentatively attributed to the liberation of other degrees of freedom of the molecule than ring reorientation, particularly those associated with the librations of the molecule as a whole.

Although the structure of the high temperature phase (stable between 305 and 315 K) has not been determined, X-Ray diffraction studies have confirmed the existence of a solid-solid phase transition around 305 K.[29]

V. RELATION BETWEEN THE CRYSTAL STRUCTURES AND THE THERMODYNAMIC FUNCTIONS

Table V gives the thermodynamic functions of a series of arene metal carbonyls we have investigated in our laboratory. In addition, some

spectroscopic data deduced from vibrational studies[4,5,7] and lattice energies obtained from crystallographic measurements[28] are also given. These results allow us to compare the thermal behaviour of these solids in terms of disorder and lattice energies.

i) We can compare complexes exhibiting an order-disorder phase transition at low temperature with those remaining ordered at 300 K. As expected, the entropy variation associated with fusion is significantly lower for compounds of the first group ($\Delta S_f \sim 55$ JK^{-1} mol^{-1} for $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$) than for compounds of the second one ($\Delta S_f \sim 40$ JK^{-1} mol^{-1} for $C_4H_4NMn(CO)_3$ and $C_4H_4PMn(CO)_3$). Nevertheless, one must keep in mind that, according to Timmerman,[36] all these compounds cannot be classified in the family of plastic crystals which have generally a ΔS_f value lower than that of the solid-solid transition ($\Delta S_f < 20$ JK^{-1} mol^{-1}).

ii) The difference between the thermodynamic functions of compounds which do not present a phase transition below the melting point requires some comments. This case concerns particularly $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$. The former has a fusion enthalpy and lattice energy[28] larger than those of the later one. Furthermore, we have shown from quasielastic neutron scattering experiments[9] and vibrational studies[5,7] that, in the solid state, the potential barriers associated with the aromatic ring reorientation have practically the same values and the average frequencies of the external modes associated with the translations and librations of $C_6H_6Cr(CO)_3$ complex are somewhat higher than those of $C_5H_5Mn(CO)_3$. This indicates that the intermolecular forces in $C_6H_6Cr(CO)_3$ are more important than in

TABLE V

Thermodynamic functions associated with solid-solid transition and fusion of $C_6H_6Cr(CO)_3$, $C_5H_5Mn(CO)_3$, $C_4H_4NMn(CO)_3$ and $C_4H_4PMn(CO)_3$. The lattice energies, enthalpies of sublimation and some spectroscopic data of the two former complexes are also given for comparison

	$C_6H_6Cr(CO)_3$	$C_5H_5Mn(CO)_3$	$C_4H_4NMn(CO)_3$	$C_4H_4PMn(CO)_3$[11]
Solid–solid transition $T(K)$			305	115
Solid–solid transition ΔH_t (J mol^{-1})			1910	480
Solid–solid transition ΔS_t (JK^{-1} mol^{-1})		< 1	6.3	4.2
Fusion $T(K)$	449	350	315	310
Fusion ΔH_f (J mol^{-1})	24900	19300	13010	12500
Fusion ΔS_f (J K mol^{-1})	55.5	55	41	40
Sublimation ΔH_S (J mol^{-1})	91120[41]	52250[40]		
Lattice energy (J mol^{-1}) (300 K)	65600[28]	60600[28]		
Average librational frequency (cm^{-1})	54[5]	49[7]		
Average translational frequency (cm^{-1})	39[5]	31[7]		

$C_5H_5Mn(CO)_3$ crystal. Nevertheless, the sublimation energies ΔH_S deduced from vapor pressure measurements of Cordes *et al.* on these compounds[40] do not agree with the above conclusion.

As shown in Table V, the reported ΔH_S value for CpMnT is, on the one hand lower than lattice energy obtained from crystallographic study[28] and on the other hand, two times smaller than the ΔH_S observed for $C_6H_6Cr(CO)_3$. The examination of Cordes *et al.* experiments shows that, for CpMnT, only three vapor pressure measurements have been performed in the temperature range 335–343 K; these experimental points being rather scattered, while for $C_6H_6Cr(CO)_3$, the ΔH_S has been confirmed by Connor *et al.*[41] So it appears that the sublimation energy of CpMnT reported by Cordes *et al.* is less than convincing and new experiments over a larger temperature range would be necessary to remove the contradiction stated above.

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