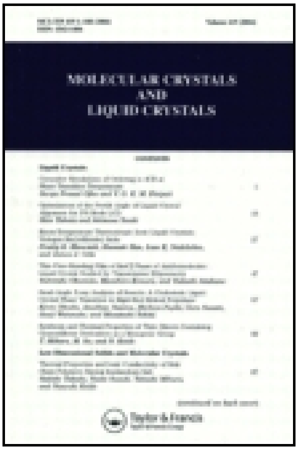

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Thermodynamic and X-Ray Studies on Arene Chromium Carbonyls

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Thermodynamic and X-Ray Studies on Arene Chromium Carbonyls

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The heat capacities of benzene chromium tricarbonyl and benzene chromium dicarbonyl thiocarbonyl have been investigated in the range 4–300 K, and the thermodynamic functions are reported. Results are compared with the C_p values calculated from spectroscopic data. Selenophene- and tellurophene-chromium tricarbonyl have been studied in the range 80–300 K by calorimetry and X-Ray diffraction. The unit cells of these last two complexes have been determined (orthorhombic, $Z = 4$) as well as the variations of the lattice parameters. No anomaly has been detected in the heat capacity curves of the four compounds. Molecular motions (ring reorientation) are discussed in the light of these results and those of Raman spectroscopic studies.

INTRODUCTION

In molecular solids such as metallocenes or arene metal carbonyls, rotational motions of the aromatic rings have been observed above a given temperature. Such a reorientation may induce disorder in the crystal and then a phase transition occurs when the temperature decreases, either as a first order structural transition (e.g. in ferrocene,[1,25] thiophene chromium tricarbonyl[2]) or as a high order transition (e.g. in nickelocene).[3,4] In both cases, these phenomena are accompanied by a configurational entropy and consequently the appearance of an anomaly of the heat capacity curves. Thiophene chromium tricarbonyl (TCT) has been reported to show an order disorder phase transition with a structure change at $T_c = 185$ K.[2] In the high temperature phase, a structure with a threefold disorder has been proposed.[5] A Raman scattering study[6] has confirmed the thermal activation of reorientational ring motion above 140 K. The experimental calorimetric and X-Ray measurements[2] are in accordance with the assumption of a completely ordered structure below 120 K and a total disorder between three equivalent distinguishable allowed ring orientations above 220 K (total configurational entropy $\Delta S = R \log 3$ in the range 120–220 K). The determination of configurational entropy $(S_{\mathrm{conf}})_T$ from heat capacity measurements allows the calculation of order parameter η. In the range of temperature mentioned above, S_{conf} is expressed by:

$$(S_{\mathrm{conf}})_T = -R[2x \log x + (1 - 2x)\log(1 - 2x)] \tag{1}$$

where $1 - 2x$ is the molar fraction of molecules in the low temperature orientation and x is the molar fraction in each of the two other orientations. The order parameter η can be defined by

$$(\eta)_T = 1 - 3x \tag{2}$$

Figure 1 shows the evolution of η in the course of transition: there is a jump at the first order transition temperature T_c, but at this point, the high temperature phase is not completely disordered.

Benzene chromium tricarbonyl (BTC) is isomorphous with TCT at 300 K. Solid state NMR studies have shown anomalous variations of the spin-lattice relaxation time and line-width with temperature at about 100 K, attributed to the rotation of the arene group around the principal molecular axis.[7] A recent Raman spectroscopic investigation[6] reveals that the aromatic ring reorientation is thermally activated in the range 100–120 K. In a previous study[2] we have reported that no anomaly was detected in the heat capacity curve between 100 and 300 K as well as in the lattice parameters evolution in the 80–300 K range.

In order to define the behaviour of BCT at low temperature, we have reinvestigated its heat capacity by more accurate adiabatic measurements. For comparison, three others arene chromium carbonyls have been studied. Benzene chromium dicarbonyl thiocarbonyl $C_6H_6Cr(CO)_2CS$, (BCD), selenophene- and tellurophene-chromium tricarbonyl (Se CT), (Te CT).

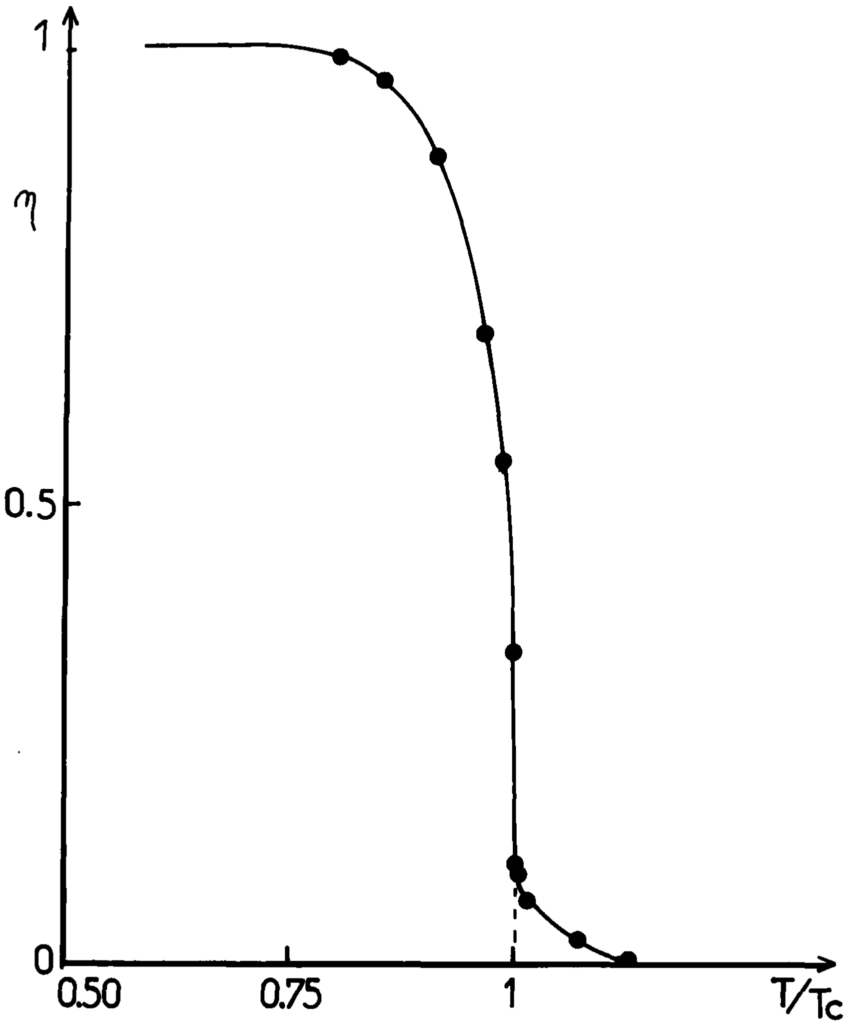

FIGURE 1 Order parameter of thiophene chromium tricarbonyl.

EXPERIMENTAL

Samples

Benzene chromium tricarbonyl is a commercially available product (Alfa Inorganics, Germany). The sample was purified by repeated sublimations in vacuum. The purity, after elementary analyses, is better than 99 %. Benzene chromium dicarbonyl thiocarbonyl was synthetized according to the method described by Jaouen *et al.* from BCT.[8] The crude product was purified by liquid chromatography and crystallizations in hexane.

Selenophene chromium tricarbonyl was prepared by reaction of the organic ligand on tricyanomethyl chromium tricarbonyl at room temperature.[9] Tellurophene chromium tricarbonyl was kindly provided by Dr K. Öfele (Munchen Technical University, Germany). These compounds are purified by crystallizations in ether and kept away of light in vacuum seals.

The purity of the three last studied samples is higher than 98%.

Calorimetric procedure

Calorimetric studies on BCT and BCD were performed on an adiabatic apparatus described elsewhere.[10] 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 thermal contact between calorimeter and sample. It was then 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 for thermal contact between calorimeter heater and thermometer. The heat capacity of the sample represented 25 to 60 percent of the total heat capacity observed. The calorimetric samples have a mass of 9.2570 g and 8.7192 g for BCT and BCD respectively. The estimated probable error is 5% below 30 K and decreases to 0.5% at 300 K.

Measurements on SeTC and TeCT were made on a differential scanning calorimeter (MCB, Arion, France)[11] which needs a much smaller amount of sample (about 300 mg). In order to increase the thermal conductivity, about 10 mg of aluminum powder were added in the sample cell. The heat capacities are determined within ±5% up to 150 K and ±3% in the 150–300 K range.

X-Ray measurements

X-Ray powder data have been obtained on a high-accuracy goniometer ($\pm 3.10^{-3\circ}\theta$) using CuKα radiation (rotating anode, 40 KV, 200 mA). The sample was placed inside a cryostat, its temperature was regulated to better than 0.5 K and measured with a silicon diode. Ten to twelve diffraction patterns were recorded in the range 78–300 K for each compound.

RESULTS

Benzene chromium complexes

The heat capacity values obtained in the low temperature adiabatic calorimeter are listed in Tables I, II in chronological order. The values are corrected for curvature and the approximate temperature increments can usually be inferred from adjacent mean temperatures.

The values of C_p, $S°(T) - S°(0)$, $H°(T) - H°(0)$ and $(G°(T) - H°(0))/T$ are listed at selected temperatures in Tables III, IV. These values were obtained from the experimental heat capacities by a least-squares-fitted curve through the experimental points. Values below 8 K were extrapolated with a Debye T^3 heat capacity function. An additional digit beyond those significant is given to permit interpolation and differentiation.

Figures 2 and 3 show the heat capacity curves in the studied temperature range.

These experimental heat capacities can be compared with estimated values obtained from spectroscopic data. The specific heat at constant volume (C_v) is calculated from the optic and the acoustic spectral branches. The heat capacity at constant pressure (C_p) is written as:[12–15]

$$C_p = (C_p - C_v) + C_v\,(\text{lattice}) + C_v\,(\text{int.}) \tag{3}$$

C_v (latt.) is usually represented by a six-fold Debye function with a Debye temperature θ_D estimated from the experimental results below 20 K, temperature range where the contributions of the two other terms to C_p (Eq. 3) are negligible. C_v (int.) is calculated using Einstein functions and internal vibration frequencies of the molecule.

The difference $C_p - C_v$ is given by the thermodynamic relation:

$$C_p - C_v = \alpha^2\, VT/\beta \tag{4}$$

However, although the molar volume V and the thermal expansion coefficient α are often known, experimental data on the compressibility factor β are very scarce. Usually, recourse is made to the quasithermodynamical results of Lord:[16]

$$C_p - C_v = [aC_v\,(\text{latt.}) + bC_v\,(\text{int.})]^2 T \tag{5}$$

where a and b are two adjustable parameters.

A recent intensive study of the Raman and IR spectra of the investigated compounds[17] especially in the low frequency range, made available the necessary data to calculate C_v (int.). Debye temperatures determined as previously mentioned were $\theta_D = 104$ K and $\theta_D = 96$ K for BCT and BCD

TABLE I

Experimental heat capacities of benzene chromium tricarbonyl

$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$
Série I		Série V		Série VIII	
121.76	114.22	19.15	13.03	8.30	2.14
127.70	117.75	23.92	25.33	13.59	7.10
132.98	121.08	26.29	30.29	18.05	14.28
138.64	124.03	29.00	35.57	21.23	20.43
144.42	128.36	31.30	39.32	23.34	24.39
150.52	131.55			25.81	29.54
157.16	137.21			28.60	34.94
163.68	139.91	Série VI		31.45	39.45
170.86	145.24	42.61	54.82	34.40	44.35
178.23	149.93	45.86	58.46	37.34	48.63
185.82	155.20	49.74	62.23	40.45	52.61
193.60	159.46	53.78	66.06	43.74	56.29
		57.53	69.53	47.24	59.14
Série II		61.45	73.16	50.98	62.78
192.01	158.81	65.97	77.46	54.93	67.08
198.33	162.96			59.04	70.34
205.54	168.03	Série VII		63.30	74.70
212.60	172.13	8.89	2.14	67.91	78.36
219.46	176.43	13.91	8.05		
226.62	182.76	18.54	16.09		
		22.43	22.77		
Série III		25.08	28.06		
251.88	200.07	28.55	35.05		
257.97	203.63	31.55	39.75		
264.02	207.66	34.57	44.56		
269.72	212.62	38.48	50.12		
275.52	217.56	42.60	54.95		
281.20	221.44	46.86	59.23		
287.59	226.93	51.18	63.42		
		55.61	67.89		
Série IV		60.23	71.92		
88.31	92.18	64.64	75.89		
92.25	94.41	69.16	78.85		
96.32	97.47	73.84	82.15		
100.83	101.00	78.62	84.51		
105.50	104.84	83.50	89.14		
110.03	107.77	88.57	90.90		
114.69	110.77				
119.54	113.65				
124.51	116.19				
129.62	119.23				
134.62	122.87				
138.24	124.36				
143.08	127.32				
147.83	131.20				
152.48	133.78				
157.05	136.38				

TABLE II

Experimental heat capacities of benzene chromium dicarbonyl thiocarbonyl

$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$
Série I		Série III		Série VII	
80.03	93.95	232.64	192.23	6.07	2.44
82.83	96.31	238.56	195.27	8.00	3.88
86.38	98.83	244.37	197.95	10.26	6.27
90.64	102.03	250.00	200.79	12.47	9.25
95.61	106.11	255.57	203.93	14.30	12.86
100.39	109.09	261.17	207.25	15.98	15.40
105.02	112.69	266.62	210.35	17.84	18.57
109.49	116.24			19.73	23.09
113.81	119.00	Série IV		21.26	26.84
119.04	123.33	159.79	150.82	22.85	30.40
125.16	127.11	169.36	157.28	24.79	34.06
131.09	131.76	174.74	162.22	26.95	38.87
136.85	135.37	181.94	165.79	29.28	42.51
141.94	138.27	188.94	169.88	31.68	47.41
146.01	141.50	195.81	173.86	34.15	51.68
149.95	143.71	202.54	177.43	Série VIII	
		209.13	179.28	31.67	47.41
Série II		215.50	183.38	34.15	51.68
157.71	149.55	221.76	187.45	36.52	53.70
165.27	154.55			38.97	57.43
172.62	159.04	Série V		41.72	60.23
179.77	163.25	271.86	212.87	44.79	63.39
186.75	167.34	276.95	215.36	48.34	66.83
193.55	172.27	281.95	217.90	51.85	69.89
200.18	174.81	286.79	220.78	55.16	73.64
213.08	183.28	291.18	222.88	58.44	76.55
219.25	185.34	295.91	225.37	61.82	79.64
225.33	188.19			65.22	82.30
231.31	190.97	Série VI		68.81	85.69
237.10	194.28	277.57	215.68	72.49	87.71
242.87	197.95	282.72	218.29	76.04	91.09
		287.73	221.27	79.45	93.59
		292.66	223.77	82.72	96.19
				86.07	98.49

respectively. Best fittings with the experimental C_p curves were obtained with

$$a = 4.10^{-3}, \quad b = -10^{-4} \quad \text{for BCT}$$

$$a = 5.10^{-3}, \quad b \cong 0 \quad \text{for BCD}$$

Results are reported on Figures 2 and 3.

TABLE III

Thermodynamic functions of benzene chromium tricarbonyl

$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\frac{S°(T) - S°(0)}{J\,K^{-1}\,mol^{-1}}$	$\frac{H°(T) - H°(0)}{J\,mol^{-1}}$	$\frac{-\{G°(T) - H°(0)\}/T}{J\,K^{-1}\,mol^{-1}}$
5	0.70	0.21	0.91	0.05
10	3.313	1.071	7.668	0.304
15	9.076	3.389	37.21	0.908
20	17.93	7.153	103.7	1.968
25	27.9	12.23	218.4	3.494
30	37.09	18.14	381.3	5.435
40	52.04	30.99	831.6	10.21
50	62.25	43.75	1405.2	15.64
60	71.84	55.95	2075.0	21.36
70	79.03	67.65	2833.9	27.16
80	86.58	78.7	3662.4	32.92
90	93.6	89.3	4563.7	38.6
100	100.2	99.51	5533.2	44.18
110	106.6	109.4	6567.8	49.66
120	112.9	118.9	7665.9	55.04
130	119.2	128.2	8826.7	60.31
140	125.5	137.3	10050	65.5
150	131.9	146.1	11338	70.57
160	138.5	154.9	12690	75.57
170	145.2	163.5	14109	80.5
180	151.9	171.9	15595	85.33
190	158.8	180.3	17149	90.11
200	165.7	188.7	18771	94.84
210	172.5	196.9	20462	99.5
220	179.2	205.1	22221	104.1
230	185.9	213.2	24047	108.7
240	192.5	221.3	25939	113.2
250	199.1	229.3	27898	117.7
260	205.9	237.2	29923	122.1
270	213	245.1	32017	126.5
273.15	215.4	247.6	32692	127.9
280	220.8	253	34186	130.9
290	229.6	260.9	36437	135.3
298.15	238.1	267.4	38342	138.8
300	240.2	268.8	38785	139.6

X-ray diffraction patterns on BCD could not be indexed in the same monoclinic cell as for BCT crystal. They are indicative of an essentially unique structure in the 80–300 K range. The evolutions of θ values for 12 typical diffraction lines versus temperature show no anomaly in this temperature range.

Selenophene and tellurophene complexes

Experimental heat capacities are displayed on Figure 4. Surprisingly no evidence of phase transition is observed, as in the thiophene chromium

TABLE IV

Thermodynamic functions of benzene chromium dicarbonyl thiocarbonyl

$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\frac{S^\circ(T) - S^\circ(0)}{J\,K^{-1}\,mol^{-1}}$	$\frac{H^\circ(T) - H^\circ(0)}{J\,mol^{-1}}$	$\frac{-\{G^\circ(T) - H^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$
5	1.885	1.609	4.198	0.770
10	6.015	4.01	22.65	1.742
15	13.53	7.75	70.10	3.080
20	23.82	13.10	162.7	4.875
25	34.72	19.51	309.3	7.135
30	44.20	26.70	507.4	9.791
40	58.15	41.52	1025.5	15.88
50	68.73	55.66	1661.3	22.43
60	77.93	69.02	2395.5	29.09
70	86.25	81.67	3217.0	35.71
80	94.04	93.70	4118.8	42.21
90	101.55	105.2	5096.9	48.56
100	108.92	116.3	6149.3	54.80
110	116.22	127.0	7275.0	60.88
120	123.47	137.4	8473.5	66.82
130	130.64	147.6	9744.1	72.65
140	137.71	157.5	11086	78.36
150	144.61	167.3	12498	83.96
160	151.30	176.8	13977	89.47
170	157.73	186.2	15523	94.89
180	163.89	195.4	17131	100.2
190	169.76	204.4	18799	105.5
200	175.37	213.2	20526	110.6
210	180.75	221.9	22306	115.7
220	185.94	230.5	24140	120.7
230	191.03	238.9	26025	125.7
240	196.08	249.1	27960	130.6
250	201.16	255.2	29946	135.4
260	206.32	263.2	31984	140.2
270	211.61	271.5	34073	144.9
273.15	213.29	273.5	34743	146.3
280	216.98	278.9	36216	149.5
290	222.37	286.6	38414	154.1
298.15	226.66	292.8	40243	157.8
300	227.61	294.2	40663	158.7

tricarbonyl.[2] The smoothed curves can be expressed by the equations:

– for SeCT, $C_p(J \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1})$

$$= 116.8 + 2{,}69.10^{-1}T + 1{,}48.10^{-3}T^2 - 2{,}08.10^{-6}T^3$$

– for TeCT, $C_p(J \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1})$

$$= 96{,}85 + 1{,}67.10^{-1}T + 2{,}44.10^{-3}T^2 - 3{,}19.10^{-6}T^3$$

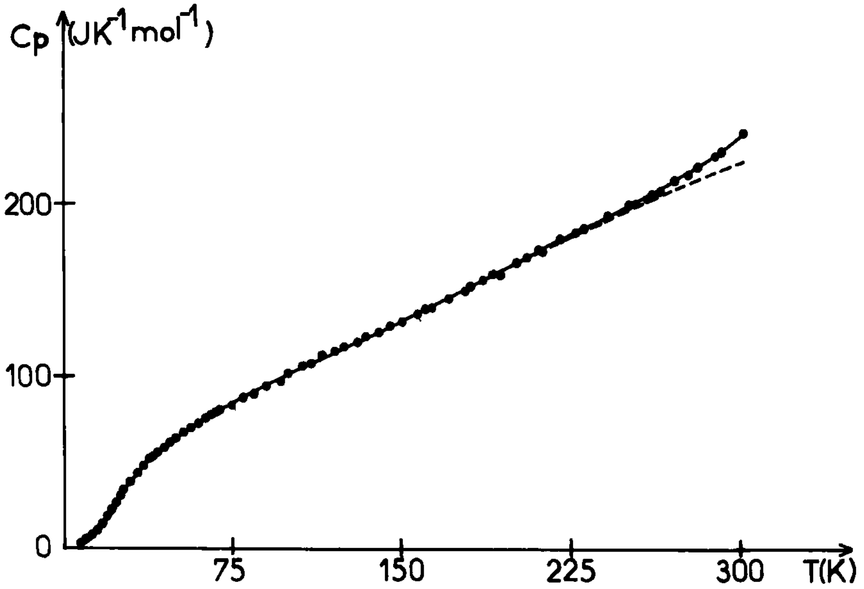

FIGURE 2 Heat capacities of benzene chromium tricarbonyl: ●, C_p (experimental); ——, C_p (cal. spectroscopic data).

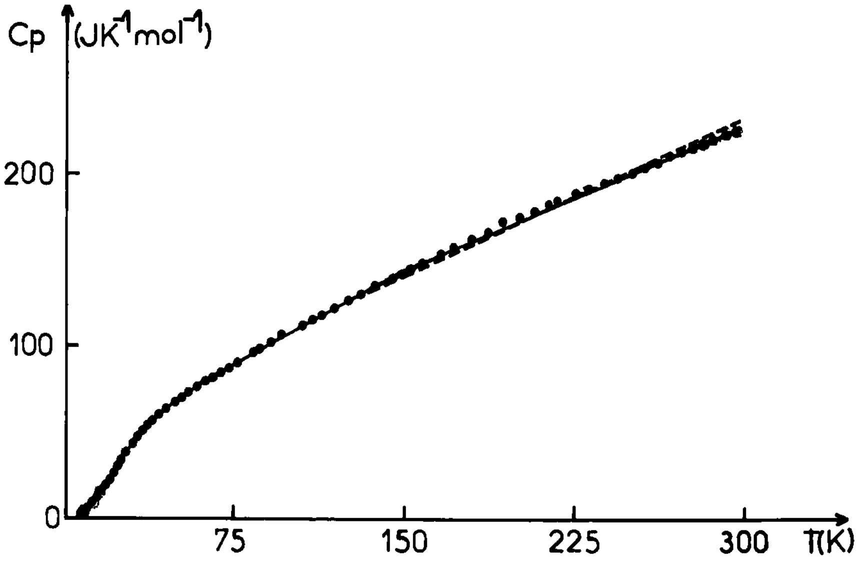

FIGURE 3 Heat capacities of benzene chromium dicarbonyl thiocarbonyl: ●, C_p (experimental); ——, C_p (cal. from spectroscopic data).

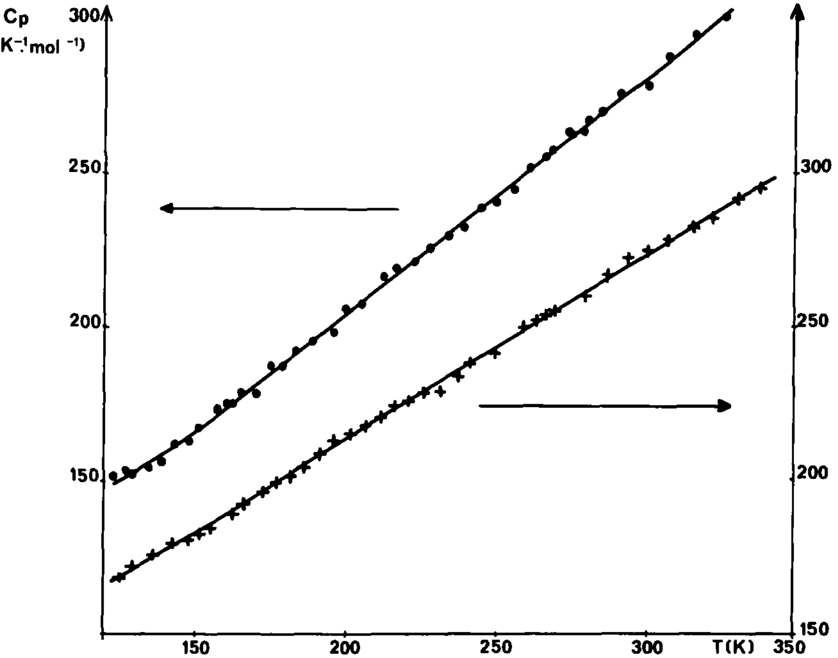

FIGURE 4 Heat capacities of selenophene—and tellurophene—chromium tricarbonyl: × Se TC, ● Te TC.

X-ray results reveal that these compounds do not crystallize in the monoclinic system as the TCT and BCT do. The diagrams have been indexed in an orthorhombic unit cell with $Z = 4$. (The cell volume is approximately twice the TCT one). The variations of the *a*, *b*, *c* parameters are normal in the range 78–300 K (Figures 5 and 6), values are given in Table V for 3 temperatures.

TABLE V

Cell parameters of selenophene—and tellurophene—chromium tricarbonyl

	Se CT			Te CT		
T(K)	78	200	295	78	200	300
a (Å)	12.188 (3)	12.228 (3)	12.277 (3)	12.449 (3)	12.515 (3)	12.588 (3)
b (Å)	9.927 (3)	9.992 (3)	10.047 (4)	9.919 (4)	9.972 (4)	10.013 (4)
c (Å)	6.732 (1)	6.791 (1)	6.840 (1)	6.863 (2)	6.918 (2)	6.968 (2)
v (Å^3)	814.4 (3)	829.8 (4)	843.7 (4)	847.4 (4)	863.4 (5)	878.8 (5)

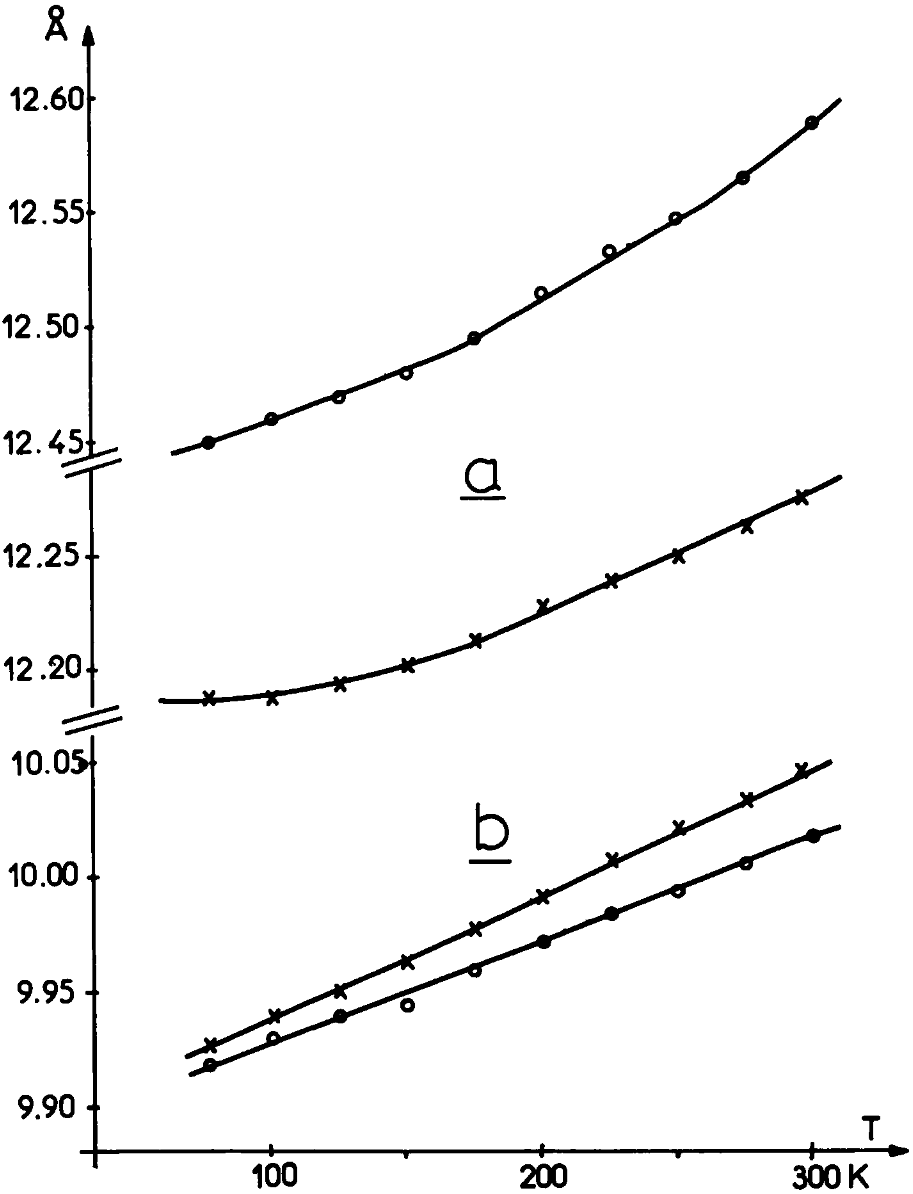

FIGURE 5 a, b cell parameters of selenophene-(×) and tellurophene-(O) chromium tri-carbonyl.

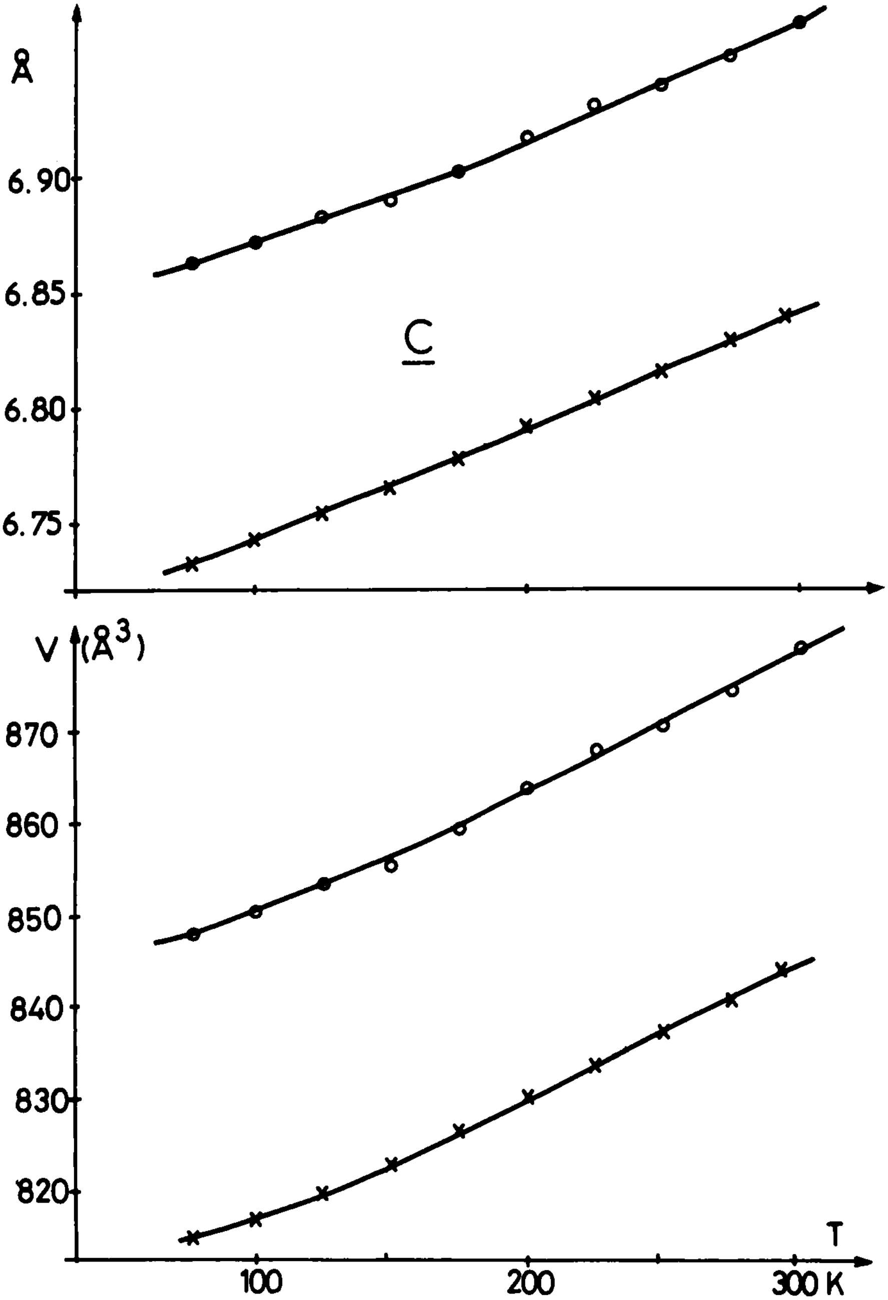

FIGURE 6 *c* parameter and cell volume of selenophene-(×) and tellurophene-(○) chromium tricarbonyl.

DISCUSSION

Benzene chromium complexes

As shown in Figure 2, the agreement between experimental and calculated curves for BCT is excellent in the whole temperature range 4–280 K and confirm the absence of a noticeable anomaly in this range. Above 280 K, the difference C_p (exp.) $-$ C_p (cal.) is about 2–5 %. For BCD, as displayed in Figure 3, the values of C_p (exp.) and C_p (cal.) show good agreement at low temperature but deviate by about 2 to 5 % above 150 K.

The benzene ring arrangement in the BCT monoclinic cell has been found staggered with respect to the carbonyl groups. No significant distorsion from the D_{6h} symmetry has been reported at 300 K.[18] A more detailed study by X-Ray and neutron diffraction at 78 K reveals a lower symmetry C_{3v},[19] the difference in the C—C bond lengths is within 0.01 Å. The NMR[7] and Raman data are in accordance with a ring rotational motion beginning at about 100 K.

As no additional entropy have been observed in the whole investigated temperature range (Figure 2), it must be concluded that the configurations introduced by the reorientational jumps of the aromatic ring around the principal molecular axis are either identical ($2\pi/6$ rotation in a D_{6h} model) or only slightly distinguishable ($2\pi/6$ rotation in C_{3v} model). In the later case, the energy difference between the ordered and disordered states will be very small and the eventual transition would occur at such a low temperature that it will not be observable for kinetic reasons.[20]

Using such a six fold potential barrier and the torsional oscillation frequency, the barrier height can be calculated:[14] 16,93 KJ · mol^{-1} at 100 K. This value agrees quite well with the activation energy reported from NMR study:[7] 17,55 KJ · mol^{-1}.

The experimental results on the BCD do not indicate any abnormal behaviour. The Raman low frequency study[17] gives a mean potential barrier energy for torsional mode $V_6 = 8{,}36$ KJ · mol^{-1}. The ring reorientational process in this compound is most probably the same as in BCT but the population of molecules with aromatic ring in the state of jump must be greater at a given temperature. However in the absence of more precise results concerning crystal structure no further comment can be made.

Selenophene and tellurophene complexes

The above results show that these compounds behave very differently from the thiophene complexe.

As mentioned previously, they crystallize in an orthohombic cell. The linear (α_a, α_b, α_c) and volumic (α_v) expansion coefficients have been calculated in various temperature ranges. Their evolution is regular and average values are reported in Table VI. α_v is similar for the two compounds but the anisotropy of the dilatation is larger for SeTC and increases as the temperature decreases. This expansion is more important and less anisotropic than for BCT and TCT for which the principal expansion coefficient is higher than $100 \cdot 10^{-6}$ K^{-1} above 100 K[2].

TABLE VI

Thermal expansion coefficients of selenophene—and tellurophene—chromium tricarbonyl ($\times$ 10^{-6} K^{-1})

	Se CTC		Te CTC	
ΔT(K)	78-175	200-295	78-175	200-300
α_a	22 (4)	42 (4)	37 (4)	58 (4)
α_b	52 (5)	58 (5)	42 (5)	46 (5)
α_c	71 (2)	74 (2)	60 (4)	72 (4)
α_v	145 (5)	174 (5)	139 (6)	176 (6)

In Table VII are reported the molecular volume in the crystal (v = cell volume/Z) for all studied compounds and for cyclopentadienyl manganese tricarbonyl (CMT).[21] In addition, we have estimated Van der Waals volume increases of the aromatic ligands compared with the C_5H_5 ring, using Van der Waals radii[22] and volume increments[23] found in the literature. It can be seen that at 78 K, temperature at which all these compounds would be ordered, the molecular volumes v increase regularly with the aromatic ligand size. It is noticeable that between 78 and 295 K, Δv % is much larger for TCT, in accordance with the phase transition.

TABLE VII

Increase of ligand Van der Waals volume (δV) and experimental molar volume of studied complexes compared with C_5H_5 $Mn(CO)_3$, (CMT)

	CMT	TCT	Se CT	Te CT	BCT
δV (Å^3)		2	6	14	13
v(78 K) (Å^3)	194.7	199.0	203.6	211.9	209.9
v (295 K) (Å^3)	206.1	216.6	210.9	219.5	219.8
Δv % (295-78 K)	5.9	8.8	3.6	3.6	4.7

The thermodynamic study on SeCT and TeCT does not reveal any thermal transformation in the range 100–300 K. However, rotational motions of the aromatic rings have been observed above 130 K from spectroscopic measurements between 4 and 300 K.[6] In order to explain the absence of configurational entropy, we have to admit that the structure remains ordered at least locally, that is the ring reorientational jumps take place with an important correlation.[24]

CONCLUSION

In the studied organometallic molecular crystals, it appears that the aromatic ligands are able to reorient above a given temperature range. The influence of such motions on the order in the crystal and the solid structure depends on the molecular symmetry and packing.

X-ray diffraction and calorimetric measurements provide useful information on the macroscopic properties dealing with order and disorder in the solid. To define the dynamics of disorder, spectroscopic data are of help.

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