Liquid Crystals

Adiabatic calorimetry of the metallomesogen purple cobalt stearate Co(O₂CC₁₇H₃₅)₂

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Adiabatic calorimetry of the metallomesogen purple cobalt stearate $Co(O_2CC_{17}H_{35})_2$

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The heat capacity of the metallomesogen purple cobalt stearate $Co(O_2CC_{17}H_{35})_2$ has been measured by adiabatic calorimetry at temperatures between 16 and 420 K. This compound exhibits two crystalline phases (low temperature Cr2 and high temperature Cr1 phases), mesophase (M phase), and isotropic liquid (I phase). A third crystalline phase Cr3, which is entirely metastable with respect to all the others, is suggested by DSC studies. The Cr2-to-Cr1, Cr1-to-M, and M-to-I phase transitions occurred at 362.1, 380.9, and 400.4 K, respectively. The enthalpy and entropy gains at these phase transitions were determined. The mesophase is either smectic A or nematic.

1. Introduction

Metal soaps, neutral or ionic compounds of metals bound or otherwise complexed to carboxylic acids, are widely known and used in many practical applications as catalysts, lubricants, and coating materials. Cobalt soaps are widely used in these practical applications also. Soaps of course are the classic examples of lyotropic mesomorphism and many heavy metal carboxylates exhibit lyotropic mesomorphism especially when the solvent is water. Moreover, some metal carboxylates exhibit thermotropic mesomorphism, the carboxylates of Cu(II) for example. The two common oxidation states of cobalt are $2+$ and $3+$ and examples of cobalt carboxylates made from Co(II) and Co(III) are well known. While many Co(II) compounds are known, very few exhibit thermotropic mesomorphism, that is, are metallomesogens. Certain cobalt phthalocyanines [1], and salts of *N*, *N'*-bis[3-(3,4-dialkoxylphenyl)-3-oxopropenyl]ethylenediamines [2] exhibit columnar mesomorphism. One cobalt soap in particular, cobalt(II) stearate, was extensively studied by Kambe and coworkers [3]. Kambe alluded to the existence of mesomorphism of cobalt stearate but did not claim the material to be a metallomesogen. Depending on reaction conditions several cobalt stearate salts may be prepared, at least one of which we recognize as a metallomesogen. We have carefully investigated the

compound referred to as blue soap by Kampe. Since the actual colour of the blue salt is much more a purplish-blue, in this article we will call this salt purple cobalt stearate. This purple salt is neutral, and analyses as a 1/2 ratio of cobalt(II) to carboxylate anion. Because of the purple colour the salt is believed to have the four oxygens of the two carboxylates providing the cobalt ion tetrahedral or distorted tetrahedral oxygen coordination. This purple cobalt stearate exhibits thermotropic mesomorphism in the range from 108 to 127°C. We report here our adiabatic calorimetric measurements on this purple cobalt stearate and comment on the complexity of the signals often obtained by power-compensated differential scanning calorimetric measurements.

2. Experimental

The synthesis of cobalt stearate was conducted by metathesis. The general procedure was to add an aqueous solution of cobalt nitrate to a neutral solution of stearic acid. Stearic acid, Aldrich 95%, was recrystallized before use from an ethanol/water mixture. The cobalt nitrate monohydrate, Aldrich 98%, was also recrystallized from water before use. The specific sample used for these calorimetric measurements was synthesized as follows. Some 2.02 g (7.03 mmol) of recrystallized stearic acid was dissolved in 100 ml of 2.5/1 ethanol/water mixture with heat and stirring. Two drops of phenolphthalein indicator were added. After cooling, the solution was brought to a 'neutral pH' by the addition of a potassium hydroxide solution to a slight

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phenolphthalein pink. Recrystallized cobalt nitrate monohydrate, 2.28 g (7.83 mmol), dissolved in a minimal amount of water, about 6 ml, was added dropwise to the stirred and heated stearic acid solution. Upon addition of the cobalt nitrate a light pink precipitate formed which on continued stirring and heating at about 60°C becomes a dark purplish blue precipitate. The product was collected by filtration and dried for a day at about 50°C. Microanalysis conducted by the Microanalysis Laboratory of Osaka University for $Co(O_2CC_{17}H_{35})_2$ gave for C: 67.94% found, 69.09% calc., H: 11.13% found, 11.27% calc., Co: 9.08% found, 9.42% calc. The cobalt analysis was based on tricobalt tetraoxide as the ashed residue.

Thermal properties were preliminarily examined by use of a differential scanning calorimeter (Perkin-Elmer: Pyris-1 DSC); optical textures were observed by a polarizing microscope (Olympus: model LK-982) with a computer-controlled heating and cooling stage (Japan High-tech Co.). DSC samples were prepared in normal sample pans in air, and in volatile sample pans sealed under helium.

Heat capacity measurements between 16 and 420 K were made with a home-built adiabatic calorimeter [4]. The mass of sample used for the calorimetry was 1.88791 g (3.01641 mmol). The sample was loaded into a thin wall quartz glass beaker with a lid; the beaker was placed in a calorimeter vessel made of gold-plated copper–beryllium to avoid direct contact of the sample to the wall of the vessel. The vessel was sealed with a small amount of helium gas to aid the heat transfer. The thermometer mounted on the calorimeter vessel was a platinum resistance thermometer (Minco Product: model S1059), with a temperature scale calibration based upon the IPTS-68. The contribution of the sample was more than 20% in the total heat capacity including those of the vessel and the glass beaker. The details of the adiabatic calorimeter and the procedure of heat capacity measurement is described elsewhere [4].

3. Results and discussion

DSC measurements typically recorded at the rate of 15 K min^{-1} showed that fresh purple cobalt stearate $Co(O_2CC_{17}H_{35})_2$ exhibits three endothermic peaks around 360, 380, and 400 K due to a solid-to-solid phase transition, crystal-to-mesophase transition, and mesophase-to-liquid phase transition, respectively. All these peaks were considerably undercooled on the cooling run. Although significant undercooling phenomena are well recognized for crystallization and often observed in solid-to-solid phase transitions, the phase transition from isotropic liquid to mesophase, such as nematic or smectic phase, rarely gives rise to remarkable undercooling. Moreover, it should be

mentioned here that the phase transitions occurring between thermotropic cubic mesophases and isotropic liquid or smectic phases always exhibit superheating and undercooling phenomena [5–8]. In cubic mesophases molecules form a higher order, labyrinth-like structure and the pseudo unit cell contains as many as a thousand molecules. The rearrangement of such a large number of molecules between a cubic mesophase and other ordinary mesophases or isotropic liquid is not facile. Although identification of the mesophase exhibited by the cobalt stearate is not definitive, the possibility of a cubic mesophase can be ruled out. Therefore, in cobalt stearate, the large undercooling found for the transition from isotropic liquid to mesophase on cooling must be related to the kinetics of molecular rearrangement due to the large viscosity caused by the existence of the long, –C$_{17}$H$_{35}$, alkyl chains.

Since a rod-like structure can be envisioned for the cobalt stearate complex, some type of calametic phase should be expected. The microscopic textures observed under polarized light have not been identifiable as any of the well known calametic phases, smectic or nematic. The birefringence of the purple cobalt stearate is very weak, when observed at all, and obscured by the dark colour of the sample. What can be deduced from polarizing microscopy is the existence of a weakly birefringent, highly viscous fluid at temperatures above melting and below the transition to the non-birefringent isotropic phase.

We should note in passing that DSC measurements conducted in normal pans gave broader peaks than measurements made with helium-sealed volatile sample pans. The inert atmosphere apparently maintains better thermal equilibrium due to the higher thermal conductivity of helium and also protects degradation of the specimen due to oxidation.

Adiabatic calorimetry for the metallomesogen Co-$(O_2CC_{17}H_{35})_2$ in the purple form was carried out at temperatures between 16 and 420 K, and the results were evaluated in terms of the molar heat capacity at constant pressure, C_p. Strictly speaking, a correction for the heat of sublimation and vaporization of the sample into the free space of the calorimeter cell should be made for heat capacities at high temperatures. However, since the vapour pressure is very small, no weight losses were ever observed on drying samples under vacuum, for example, and since the free space in the cell was also small we neglected this correction. The thermal relaxation time required for thermal equilibration after an energy supply to the calorimeter cell was quite normal except for the phase transition regions, where it was considerably lengthened, implying the phase transitions are of first order. The measured molar heat capacities are listed in table 1 and plotted in

Table 1. Molar heat capacities of the metallomesogen $Co(O_2CC_{17}H_{35})_2$.

| $\dfrac{T}{K}$	$\dfrac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{C_p}{J\,K^{-1}\,mol^{-1}}$		$\dfrac{T}{K}$	$\dfrac{C_p}{J\,K^{-1}\,mol^{-1}}$
16.025	29.85	103.265	409.26	258.154	830.38	369.596	2117.2
18.510	37.29	105.735	418.33	261.155	838.91	370.650	2230.8
20.415	45.71	108.161	425.13	264.140	854.98	371.687	2356.0
21.988	53.32	110.857	431.95	267.110	863.59	372.700	2606.6
23.345	60.24	113.815	438.60	270.065	874.94	373.680	2946.4
24.550	65.38	116.717	442.21	273.003	885.58	374.629	3455.8
25.901	71.23	119.570	451.48	275.924	897.59	375.531	4048.1
26.916	76.22	122.376	458.82	278.823	913.11	376.427	4976.2
27.858	79.45	125.139	465.57	281.702	919.38	377.197	5901.7
28.874	85.88	127.862	472.87	284.575	925.90	377.912	6789.7
30.087	92.56	130.548	479.46	287.436	946.31	378.596	7435.1
31.445	99.41	133.199	485.68	290.258	960.53	379.196	8257.9
32.808	106.45	135.816	494.21	293.048	952.37	379.759	9189.1
34.063	113.21	138.404	500.99	295.854	961.91	380.264	11811
35.232	117.34	141.158	508.92	298.674	990.25	380.630	24596
36.329	123.15	144.072	513.86	301.482	1004.6	380.870	32785
37.366	127.59	146.955	519.57	304.368	1011.5	381.099	27535
38.349	134.29	149.805	526.06	307.332	1033.0	381.381	19744
39.283	139.15	152.625	529.08	310.287	1040.4	381.763	12631
40.181	142.78	155.417	538.34	313.229	1060.5	382.295	7369.5
41.040	148.70	158.179	545.26	316.157	1074.7	382.992	4751.8
41.868	151.64	160.917	551.62	319.072	1092.6	383.872	2482.1
42.666	157.25	163.632	557.08	320.972	1099.7	384.932	1378.5
43.577	160.85	166.322	565.08	323.018	1111.6	386.057	1398.7
44.663	168.61	168.990	571.93	325.059	1127.0	387.191	1384.0
45.910	172.11	171.637	579.51	327.601	1141.1	388.334	1417.9
47.231	180.44	174.263	584.67	330.635	1169.1	389.474	1417.2
48.491	187.63	176.869	592.65	335.648	1204.9	390.610	1425.1
49.699	194.48	179.457	597.75	337.641	1217.3	391.743	1436.2
51.045	201.20	182.026	605.59	340.618	1250.7	392.821	1434.8
52.523	206.51	184.578	612.53	342.555	1236.1	393.846	1446.8
54.027	216.09	187.113	618.64	343.516	1261.2	394.861	1537.0
55.561	223.26	189.632	624.69	344.525	1254.7	395.880	1615.1
57.221	230.81	192.135	631.12	345.535	1271.3	396.886	1711.2
59.193	240.57	194.764	637.97	346.543	1265.4	397.881	1783.2
61.268	249.97	197.518	641.89	347.550	1282.9	398.865	1891.8
63.250	258.32	200.256	645.91	348.555	1288.1	399.832	2024.6
65.152	267.03	201.448	657.89	349.558	1294.6	400.791	2023.3
66.983	274.40	204.410	664.20	350.559	1299.8	401.760	1869.6
68.753	282.48	207.353	675.42	351.560	1316.7	402.754	1617.6
70.468	289.36	210.276	681.37	352.558	1310.8	403.771	1508.5
72.134	296.33	213.183	690.42	353.554	1335.2	404.793	1494.7
73.755	303.21	218.952	706.58	354.548	1337.9	405.818	1483.6
75.336	310.23	221.809	714.24	355.792	1359.2	406.838	1494.7
77.043	315.76	224.649	725.30	357.292	1380.4	407.859	1482.1
78.955	323.70	227.475	729.99	358.531	1410.1	409.129	1501.0
81.138	331.65	230.285	741.29	359.748	1563.5	410.645	1509.7
83.497	340.17	235.879	759.32	361.053	1801.3	412.161	1490.5
85.886	348.70	238.645	764.83	362.092	3790.1	413.675	1514.5
88.309	356.27	241.398	770.59	363.078	2505.5	415.185	1511.8
90.670	364.20	244.137	782.02	364.106	1940.5	416.694	1524.5
92.973	372.28	246.864	788.95	365.204	1928.6	418.203	1511.9
95.538	383.13	249.578	799.55	366.391	1919.1	419.711	1527.1
98.172	391.61	252.278	807.90	367.431	1928.2		
100.745	400.14	255.137	818.56	368.525	2030.9		
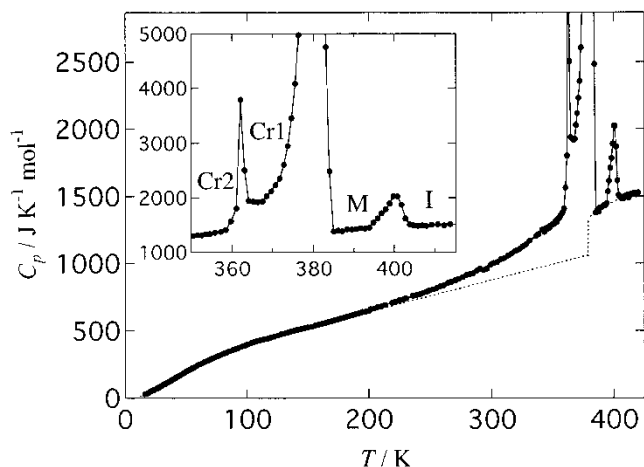
Figure 1.   Molar heat capacity of the metallomesogen purple cobalt stearate $Co(O_2CC_{17}H_{35})_2$. Broken curves indicate the normal heat capacities. Crystalline phases, mesophase, and isotropic liquid are abbreviated as Cr2, Cr1, M and I, respectively.

Figure 2.   Comparison of the molar heat capacity of the metallomesogen $Co(O_2CC_{17}H_{35})_2$ (solid circles) with the heat capacity of two moles of stearic acid $H_{35}C_{17}CO_2H$ (open circles).

figure 1. As seen in figure 1, two crystal phases (Cr2, Cr1), a mesophase (M), and an isotropic liquid phase (I) were observed by adiabatic calorimetry. The transition temperatures were determined to be 362.09 K (Cr2→Cr1), 380.87 K (Cr1→M), and 400.41 K (M→I).

Since the main part of the present complex Co-$(O_2CC_{17}H_{35})_2$ consists of two moles of the moiety stearic acid (or octadecanoic acid: $C_{17}H_{35}CO_2H$), comparison of the present heat capacity with that of the stearic acid seems to be of interest. The heat capacity of stearic acid has been reported in the 100–355 K temperature range [9]. Making an assumption of the additivity of heat capacity, the heat capacity of the present complex is compared with the heat capacity of two moles of stearic acid in the range 100–355 K in figure 2. The excellent agreement between the two data sets in the 100–355 K range demonstrates that the heat capacity of the complex is dominated by, if not completely due to, the stearate alkyl chains. As the stearic acid crystal melts at 342.5 K and its heat capacity exhibits the premelting effect, comparison at temperatures above 300 K has no meaning.

For determination of the excess heat capacities due to the phase transitions, it is necessary to estimate normal heat capacity curves or lattice heat capacity, C_{lat}. The normal heat capacity curve of the crystalline phases (Cr2 and Cr1) was determined on the basis of the effective frequency distribution method [10]. For determination of the $C_{lat}(Cr1, Cr2)$, we used 91 C_p values in the 16–200 K temperature range. A normal heat capacity curve common to the M and I phases was assumed to
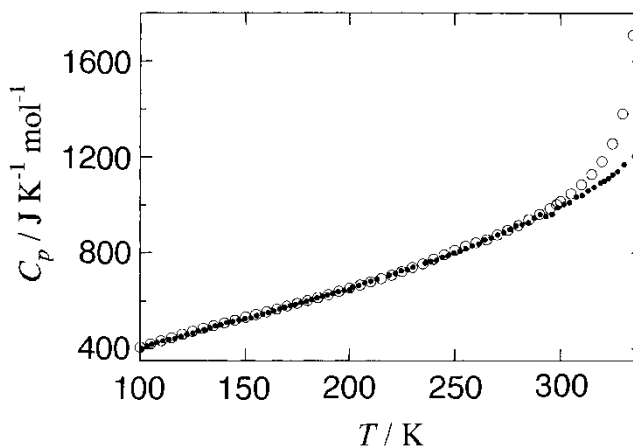
be given by a polynomial function of temperature

$$C_{nor}(M,I) = a + bT + cT^2.$$

The curve was determined by the least squares fitting 20 C_p values in the 384–420 K range except for the data lying in the 394–405 K range which are influenced by the phase transition. The estimated normal heat capacity curve is given by the following equation:

$$C_{nor}(M,I)/J K^{-1} mol^{-1} = -12620 + 66.27(T/K) \\ -0.07763(T/K)^2. \quad (1)$$

The best $C_{lat}(Cr1, Cr2)$ and C_{nor} curves thus determined are shown in figure 1 by dashed curves. The enthalpy $\Delta_{trs}H$ and entropy $\Delta_{trs}S$, gained at the phase transitions, are estimated by integrating the excess heat capacities beyond the normal heat capacity curves with respect to T and $\ln T$, respectively. For the Cr2 the integration limits were from 200 K to the Cr2 to Cr1 transition temperature 362.1 K. For Cr1 the limits were from 362.1 to 380.9 K. The values determined are summarized in table 2 and shown in figures 3 and 4. The cumulative entropy change was 298.4 J K^{-1} mol^{-1}, of which a large part (75%) was due to the melting,

Table 2.   Enthalpy and entropy gained at the phase transitions in $Co(O_2CC_{17}H_{35})_2$.

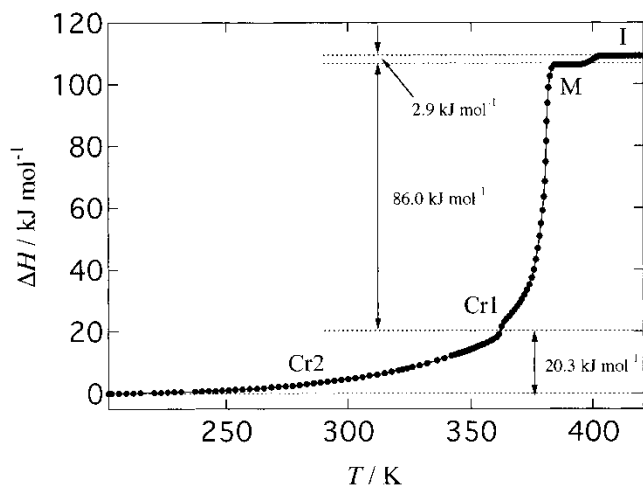| Transition	$\dfrac{T_{trs}}{K}$	$\dfrac{\Delta_{trs}H}{KJ\,mol^{-1}}$	$\dfrac{\Delta_{trs}S}{J\,K^{-1}\,mol^{-1}}$
Cr2→Cr1	362.1	20.3	63.4
Cr1→M	380.9	86.0	227.7
M→I	400.4	2.9	7.3
		Total entropy gain	298.4

Figure 3. Cumulative transition enthalpy for the metallomesogne $Co(O_2CC_{17}H_{35})_2$.
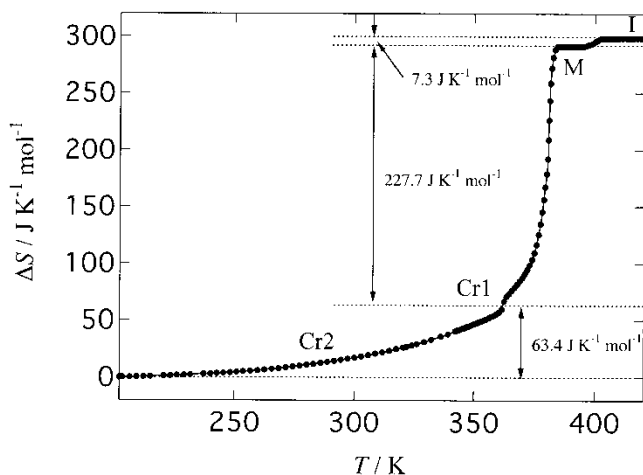

Figure 4. Cumulative transition entropy for the metallomesogen $Co(O_2CC_{17}H_{35})_2$.

while the entropy change of the phase transition occurring in the solid state (Cr2 to Cr1) was only 20%. We note that this relatively low percentage is in sharp contrast to discotic mesogens [11–15] and cubic mesogens [5–8], in which a large percentage of the entropy change comes from solid-to-solid phase transition(s). The enthalpy of the mesophase-to-isotropic liquid transition was only $2.9\,kJ\,mol^{-1}$. This value is within the range of transition enthalpy for nematic-to-isotropic liquid and smectic A-to-isotropic liquid transitions for calamitic liquid crystals [16]. Therefore, it is very likely that the mesophase manifested by the present material is either a smectic A or a nematic phase.

Since the present cobalt stearate $Co(O_2CC_{17}H_{35})_2$ consists of two alkyl chains $2 \times [-C_{17}H_{35}]$ and a core $[Co(O_2C-)_2]$, the cumulative transition entropy may be

roughly compared to the entropy gain at the melting for two moles of stearic acid $[H_{35}C_{17}COOH]$. As listed in table 2, the sum of the transition entropy amounts to $298.4\,J\,K^{-1}\,mol^{-1}$, while the entropy of fusion of two moles of stearic acid is reported to be $(356.2 \pm 1.2)\,J\,K^{-1}\,mol^{-1}$ [9]. The origin of the cumulative entropy is mainly the conformational disordering of the alkyl moieties, the so-called gauche-trans-type kinking. In a previous paper [11], we estimated the entropy contribution from a terminal methyl and methylene groups in an alkyl chain and a core of a discotic mesogen: $\Delta S(-CH_3) = 7.56\,J\,K^{-1}\,mol^{-1}$, $\Delta S(-CH_2-) = (10.31 \pm 0.53)\,J\,K^{-1}\,mol^{-1}$, and $\Delta S(core) = (38.5 \pm 3.1)\,J\,K^{-1}\,mol^{-1}$. If one simply applies these contributions to the present compound, the total entropy gain is expected to be $2\Delta S(-CH_3) + 32\Delta S(-CH_2-) + \Delta S(core) = (376 \pm 17)\,J\,K^{-1}\,mol^{-1}$. The fact that the observed transition entropy of the present compound is about 20% lower than those two estimates seems to imply that the short range order in the isotropic liquid state is stronger in the present metallomesogen than in stearic acid.

Let us now return to a further discussion of DSC measurements. Our discussion here stems from extensive DSC studies on purple cobalt stearate at heating and cooling rates varying from 5 to $30\,K\,min^{-1}$. The simple comment to make is that the DSC behaviour is complex and very dependent of sample history. While it is true that reproducible first heating thermograms exhibited thermal events around 370, 380, and 400 K, annealing and reheating experiments almost always yielded much more complex thermograms. The DSC shown in figure 5 (*a*) illustrates typical heating of a fresh
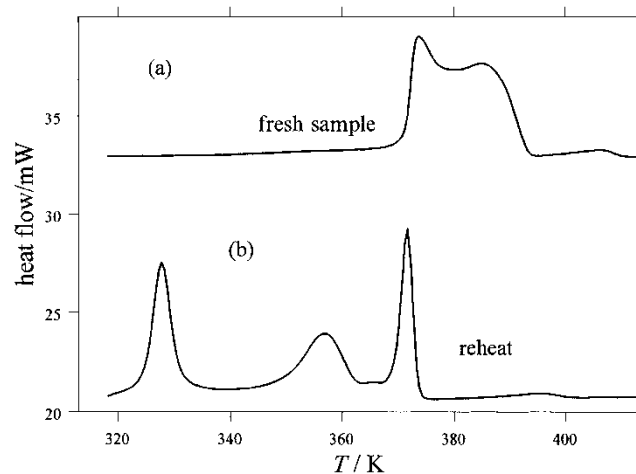

Figure 5. (*a*) DSC thermogram for a fresh purple cobalt stearate sample at $15\,K\,min^{-1}$. The scale for this thermogram has been offset $+15\,mW$. (*b*) DSC thermogram for a reheated (after cooling) purple cobalt stearate at $15\,K\,min^{-1}$. Volatile sample pans sealed under helium were used for these measurements.

sample of purple cobalt stearate. On reheating, how-ever, a new thermal event occurs around 320 K. A typical reheating DSC is illustrated in figure 5(*b*) which clearly shows a peak around 320 K. The normal thermal behaviour can be described in terms of the Gibbs energy driving forces using the qualitative curves in figure 6 for Cr1, Cr2, M, and I. A fresh sample is essentially Cr2 which transforms at 362 K to Cr1, which in turn forms M at 380 K and goes to I at 400 K. The preparative scheme used appears to yield Cr2 as the preferred crystal. The additional line in figure 6, that for Cr3, describes a crystal phase that is always metastable with respect to all other phases [except Cr1 below about 320 K]. Taking this line into account we can understand the thermogram illustrated in figure 5(*b*). Suppose on cooling below 320 K, a mixture of Cr3 and Cr1 is formed from undercooled Cr1, or perhaps even Cr3 is formed from undercooled M at point **a**; in such a case the expected heating thermogram should describe the phrase transitions: Cr3-to-Cr1 at 320 K, Cr1-to-M at 380 K, and M-to-I at 400 K. If Cr3 were superheated to
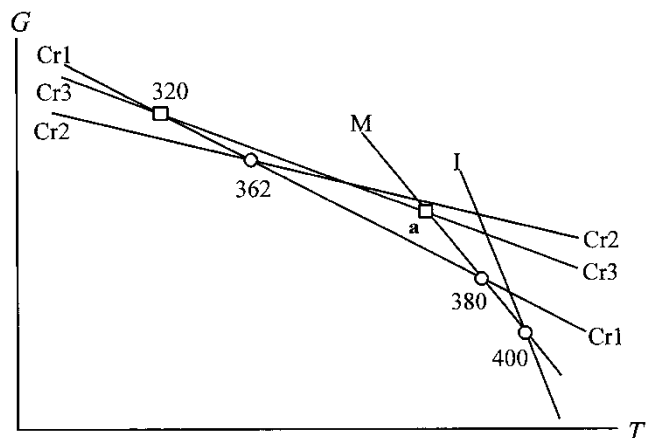

Figure 6. Suggested qualitative isobaric Gibbs energy – temperature diagram for purple cobalt stearate.

point **a**, the transition Cr3-to-M would add its energy to the DSC signal. The temperature at **a** must be less than 380 K but more than 362 K. Both the meso-morphic and the isotropic phases of purple cobalt are quite viscous, and by the arguments made above, phase

Table 3. Standard thermodynamic functions for $Co(O_2CC_{17}H_{35})_2$ at selected temperatures. The values in parenthses are those estimated by extrapolation.

$\dfrac{T}{K}$	$\dfrac{C_{p,m}^\circ}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{S_m^\circ(T)}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{\{H_m^\circ(T)-H_m^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{-\{G_m^\circ(T)-H_m^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$
10	(9.32)	(3.218)	(2.405)	(0.813)
20	43.88	19.703	14.114	5.588
30	92.08	46.376	31.881	14.495
40	142.04	79.697	53.156	26.541
50	195.95	117.163	76.307	40.857
60	244.23	157.160	100.283	56.877
70	287.48	198.088	123.966	74.122
80	327.51	239.151	146.957	92.194
90	361.95	279.765	168.997	110.769
100	397.67	319.790	190.121	129.670
120	452.60	397.609	229.713	167.896
140	505.59	471.263	265.237	206.026
160	549.49	541.495	297.888	243.607
180	599.41	609.089	328.613	280.475
200	645.53	674.903	358.262	316.641
220	709.67	739.772	387.610	352.162
240	767.67	804.120	416.961	387.159
260	835.63	868.192	446.503	421.689
280	915.67	933.029	477.136	455.893
300	997.04	998.553	508.667	489.886
320	1096.0	1065.89	542.123	523.765
340	1243.8	1136.37	578.667	557.701
360	1609.3	1211.57	619.659	591.907
		phase transition from Cr2 to Cr1 at 362.1 K		
380	10441	1389.92	761.884	628.037
		phase transition Cr1 to M at 380.9 K		
400	2024.4	1578.64	905.441	673.194
		phase transition from M to I at 400.4 K		
298.15	984.99	922.419	505.679	486.740

transitions involving these phases as well as the crystalline phases are kinetically slow, allowing super-heated and undercooled phases to be realized. In fact once the sample becomes a mixture of crystals, the DSC signals become very complex as a wide variety of phase transitions involving metastable phases occur. Since the DSC technique is a dynamic measurement, definitive DSC studies will probably remain an unanswered challenge due to the nature of the phases exhibited by cobalt stearate. However, since the adiabatic calorimetric experiment is a long-time, equilibrium experiment, and since Cr3 is metastable with respect to all phases, we should not expect to observe any adiabatic calorimetric signals involving Cr3 transitions. Thus we can understand our adiabatic results simply in terms of the equilibrium stable Cr2, Cr1, M, and I phases.

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