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The Effect of Inclusion on the Heat Capacities of Some Simple Molecules in Adducts of Dianin's Compound*

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Abstract. *The heat capacities of unsolvated ('empty') Dianin's compound (4-p-hydroxyphenyl-2, 2, 4-trimethylchroman) and the ethanol and carbon tetrachloride adducts of Dianin's compound have been measured in the 30–300 K temperature range. The molar heat capacities of the guest species were calculated from the experimental results and compared with molar heat capacities of bulk CCl_4 and bulk C_2H_5OH. The stoichiometry of the CCl_4 adduct was determined to be six host molecules per guest CCl_4, in contrast to an earlier report.*

Key words. *Dianin's compound, heat capacity, thermal properties.*

1. Introduction

4-*p*-hydroxyphenyl-2,2,4-trimethylchroman (**1**) was first found in 1914 to be capable of retaining organic solvents in fixed amounts [1]; we now know this is to be due to enclathration and we call **1** Dianin's compound, after its discoverer.

Dianin's compound has been found to include more than fifty guest molecules [2]. The general structure of the host lattice consists of hexamers of **1** stacked on each other, linked by a network of hydrogen bonds involving the hydroxy groups. This gives hourglass-shaped cages, as shown schematically in Figure 1. The cage diameter is 2.8 Å at the narrowest (the hydrogen-bonding region), 4.2 Å at the waist and 6.3 Å at the broadest point [3]. The space group for the host lattice is commonly $R\bar{3}$, and the usual host : guest ratio is either 3 : 1 (two guests per hexamer host cage; small guest molecules) or 6 : 1 (one guest per hexamer host cage; larger guest molecules). However, other ratios such as 7 : 1 (one vacancy in every seventh cage) are also observed [4].

In general, investigations of clathrates afford the opportunity to compare various properties of diluted guest molecules with their properties in their pure (bulk) form, and Dianin's compound and its clathrates are no exception. For example, Dianin's compound can enclathrate globular molecules such as CCl_4 which, in their bulk form, undergo orientational order–disorder phase transitions. In the specific case of CCl_4, this transformation is driven primarily by octupole–octupole interactions, and the potential of this interaction decays as r^{-7}, where r is the distance between the molecular centers. These phase transformations are known to be cooperative in nature, and therefore they should show a strong concentration dependence. Taking these factors together, it is interesting to 'implant' the CCl_4 molecules in a host

* Dedicated to Dr D. W. Davidson in honor of his great contributions to the sciences of inclusion phenomena.

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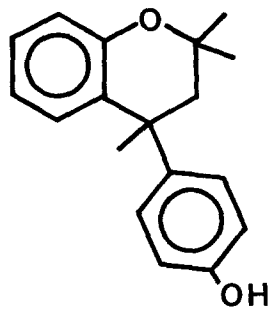

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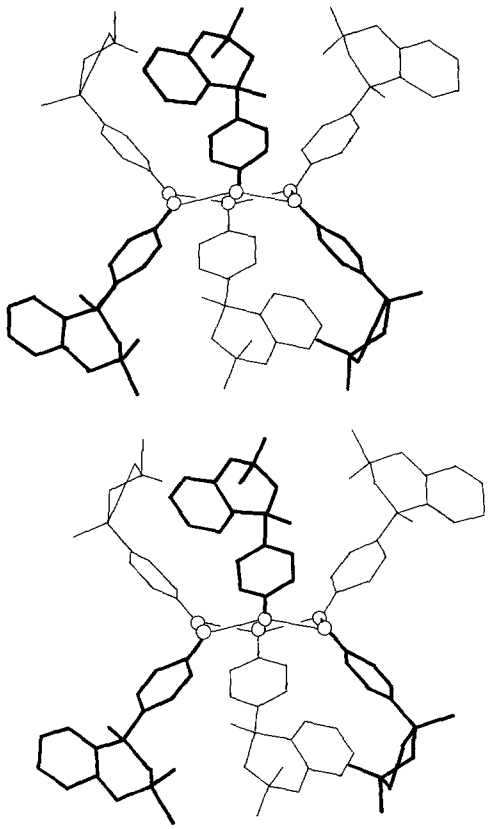

Fig. 1. A schematic view of the structure of the host lattice [3]. The phenolic oxygens are shown as open circles and the phenolic protons are omitted for clarity.

matrix and look for evidence of phase transitions. An example of a greatly-altered order–disorder phase transition on enclathration is H_2S in the hydroquinone–hydrogen sulfide clathrate [5]. Of course the cage force field also plays an important role in the determination of the properties of the enclathrated guest; in the adducts of Dianin's compound the guest–host interactions are weak.

One further especially favourable feature of Dianin's compound is that it not only forms many stable clathrates, but the host lattice also is stable [2]. This is not always the case for inclusion compounds; investigators of clathrate hydrates, for example, regularly lament the thermodynamic instability of the empty host lattice [6, 7]. Therefore, investigations of Dianin's compound permit an examination of the additivity of the guest and host properties, with a particular view to contributing to the discussion of other clathrates in which the empty host is unobservable.

The present results describe the investigation of the heat capacity of three compounds – the unsolvated ('empty') Dianin's compound (**1**), the ethanol adduct of Dianin's compound, and the carbon tetrachloride adduct of Dianin's compound – as a function of temperature. In general, properties of Dianin's compound have not been investigated thoroughly; this paper presents a preliminary report of some of the thermal properties of these materials.

2. Experimental

Dianin's compound, 4-*p*-hydroxyphenyl-2,2,4-trimethylchroman, **1**, was prepared by the reaction of phenol and mesityl oxide [2], which gave the ethanol adduct on recrystallization from ethanol. Dissolution of the ethanol adduct in concentrated base, followed by the addition of CO_2(g) gave the unsolvated ('empty') Dianin's compound [2]. The carbon tetrachloride adduct was prepared by recrystallization of the unsolvated compound in CCl_4 [2]. The observed melting points of the empty, ethanol and carbon tetrachloride adducts of Dianin's compound were, respectively, 158–159°C (157.5°C), 165°C (163–164°C) and 159–160°C (159–160°C), where the parenthetic values are from the literature [2]. Results of chemical analyses are given in Table I. The unsolvated Dianin's compound and the CCl_4 adduct were fine white powders; the ethanol adduct was colourless needles.

Table I. The results of chemical analyses for Dianin's compound (**1**), its ethanol adduct and its carbon tetrachloride adduct. The values in parentheses are theoretical values based on 3 : 1 host : guest stoichiometry for the ethanol adduct and 6 : 1 host : guest stoichiometry for the CCl_4 adduct. All values are mass per cent. Errors quoted indicate the range of duplicate analyses.

	C	H	Cl
Unsolvated Dianin's compound	79.75 ± 0.05 (80.6)	7.6 ± 0.1 (7.51)	
Ethanol adduct of Dianin's compound	79.5 ± 0.2 (79.1)	7.8 ± 0.2 (7.76)	
CCl_4 adduct of Dianin's compound	73.45 ± 0.2 (74.3)	7.1 ± 0.1 (6.86)	9.5 ± 0.1 (8.04)

The heat capacities of each of the three compounds (m(unsolvated) = 1.396 g; m(ethanol adduct) = 3.269 g; m(CCl_4 adduct) = 1.700 g) were measured from 30 K to above 300 K in an adiabatic heat-pulse calorimeter, which is described in detail elsewhere [8]. Briefly, the heat capacity measurements were made by the addition of a measured quantity of energy to the sample which was in a sealed vessel and isolated thermally from its surroundings. The heat capacity was calculated from the observed temperature rise, and the measured heat capacity of the empty vessel. Adiabatic conditions were achieved by suspension of the sample vessel within a temperature-matched adiabatic shield, all placed within a vacuum ($P < 10^{-5}$ Torr). The overall accuracy of the calorimeter, from measurement of a Calorimetry Conference standard sample of benzoic acid, is known to be $\pm 0.5\%$ [8]. The contribution of the heat capacity of each sample was about 60% of the total (sample plus vessel) heat capacity throughout the temperature region examined.

3. Results and Discussion

Chemical analyses (Table I) confirm the composition of the unsolvated Dianin's compound. In addition, they are consistent with a composition of three host molecules for each guest species in the ethanol adduct, as determined by Baker *et al.* [2] and confirmed by X-ray crystallography [3]. Our chemical analyses of the CCl_4 adduct indicate that its stoichiometry is close to 6 : 1 (host : guest). This contradicts the early findings of Baker *et al.* [2], where it was supposed to be 3 : 1. (However, the authors of Ref. 2 drew this conclusion on the basis of Cl analysis alone, and the theoretical Cl content given there is incorrect.) A recent X-ray diffraction study of the CCl_4 adduct of Dianin's compound [9] confirms that the stoichiometry is indeed 6 : 1, i.e. one guest per cage.

It is informative to set out what is known about the guests within these and similar compounds. The ethanol adduct contains one hydrogen-bonded ethanol dimer within each hexamer cage of Dianin's compound, as shown by X-ray crystallography [3] and infrared difference spectroscopy [10]. The position of each ethanol molecule is triply-degenerate, as deduced from the three-fold rotational symmetry of the crystal [3]. The large thermal parameters of the ethanol guest molecules in the X-ray study indicate motion of the guest molecules, and possibly also partial occupancies. (Chemical analyses are rather insensitive to guest composition in the ethanol adduct; however, loss of mass on heating indicates a stoichiometry close to 3 : 1. [2].)

The structure of the CCl_4 adduct of Dianin's compound is $R\bar{3}$ [9], i.e. the same as that of the ethanol adduct [3] and the unsolvated Dianin's compound [4]. It is known that there is one CCl_4 per host lattice cage [9], and that there is always a Cl 'foot' in the waist of the cage at room temperature [9]. ^{35}Cl NQR studies have shown two resonances – one from the single chlorine on the threefold axis (this is the one in the waist) and another more intense resonance from the remaining three chlorines [11]. A further interesting fact is that the CCl_4 adduct of the thiol analogue (**1** with —OH replaced with —SH) has the $R\bar{3}$ structure with *two* CCl_4 molecules per cage of six host molecules [12].

The heat capacities for each of the three compounds investigated are given in Tables II to IV, on a unit mass basis. No thermal history effects were noted, and the

Table II. The experimental heat capacities of unsolvated Dianin's compound (1)

T/K	C_p/(J K^{-1} g^{-1})	T/K	C_p/(J K^{-1} g^{-1})
47.48	0.206	189.10	0.825
52.45	0.221	190.15	0.829
57.57	0.258	195.44	0.857
63.11	0.287	197.05	0.869
69.04	0.308	198.14	0.865
74.80	0.345	203.44	0.888
82.22	0.366	205.05	0.899
82.32	0.374	206.18	0.906
88.21	0.387	211.46	0.940
97.02	0.431	213.04	0.950
99.97	0.429	214.22	0.952
103.48	0.453	219.48	0.987
105.78	0.463	221.04	0.990
105.99	0.465	222.27	0.990
109.34	0.477	227.54	0.998
111.57	0.492	229.03	1.017
111.89	0.493	230.29	1.026
116.14	0.509	235.60	1.047
118.32	0.509	237.00	1.053
123.95	0.524	238.34	1.057
126.05	0.546	244.94	1.084
131.77	0.573	246.36	1.086
133.87	0.578	252.91	1.119
134.48	0.581	254.44	1.128
139.63	0.604	259.72	1.144
141.70	0.619	260.88	1.151
142.37	0.622	262.46	1.168
147.53	0.642	267.79	1.177
149.55	0.647	268.89	1.181
150.28	0.658	275.87	1.204
155.49	0.676	276.82	1.223
157.42	0.695	283.99	1.232
158.21	0.687	284.82	1.254
163.47	0.707	285.12	1.285
165.29	0.716	286.09	1.264
166.17	0.723	292.76	1.283
171.46	0.749	293.99	1.299
173.21	0.756	294.88	1.285
174.14	0.757	308.19	1.320
179.46	0.784	315.62	1.348
181.16	0.794	323.64	1.395
182.14	0.797	325.95	1.430
187.46	0.822	334.05	1.446
		339.73	1.486

results are given in order of increasing temperature. The relaxation times following heating, which can sometimes indicate unusual thermal properties, were typical for well-behaved materials in this calorimeter, about 15 to 25 min for the empty Dianin's compound, 15 to 20 min for the ethanol adduct and 15 to 30 min for the CCl_4 adduct. In each case the shortest relaxation time was observed at the lowest temperature.

Table III. The experimental heat capacities of the ethanol adduct of Dianin's compound (1)

T/K	C_p/(J K^{-1} g^{-1})	T/K	C_p/(J K^{-1} g^{-1})
26.60	0.120	179.81	0.851
29.52	0.159	184.61	0.875
31.45	0.173	187.52	0.888
32.55	0.168	192.34	0.915
33.23	0.178	195.22	0.926
34.72	0.179	200.11	0.948
36.10	0.182	202.93	0.963
37.91	0.187	207.91	0.990
38.16	0.189	210.66	1.004
42.50	0.217	215.75	1.025
47.36	0.243	218.40	1.040
52.36	0.262	223.57	1.061
57.44	0.294	226.16	1.078
62.43	0.319	231.46	1.092
67.40	0.338	234.02	1.101
72.42	0.362	239.33	1.136
77.45	0.392	241.92	1.137
83.19	0.413	247.22	1.162
84.51	0.422	249.89	1.172
86.81	0.427	255.11	1.192
88.14	0.432	257.90	1.205
89.80	0.438	259.24	1.215
92.50	0.454	263.03	1.224
94.53	0.461	264.36	1.240
98.12	0.478	265.87	1.242
99.92	0.485	270.98	1.259
103.75	0.506	271.91	1.261
105.93	0.510	273.14	1.275
109.39	0.532	273.87	1.270
111.97	0.543	278.91	1.293
115.98	0.562	279.86	1.297
118.76	0.570	281.80	1.307
123.56	0.590	286.81	1.343
126.35	0.604	287.79	1.347
131.17	0.627	289.75	1.356
133.95	0.639	294.72	1.372
138.75	0.661	295.69	1.382
141.57	0.676	302.65	1.407
146.38	0.701	303.61	1.412
149.18	0.714	304.81	1.421
153.98	0.736	311.55	1.445
156.81	0.747	312.78	1.456
161.61	0.767	320.85	1.493
164.44	0.784	324.92	1.522
169.27	0.804	327.68	1.523
172.12	0.816	332.97	1.549
176.94	0.839	337.28	1.574
		341.02	1.586

Table IV. The experimental heat capacities of the CCl_4 adduct of Dianin's compound (**1**)

T/K	C_p/(J K^{-1} g^{-1})	T/K	C_p/(J K^{-1} g^{-1})
33.62	0.139	157.28	0.672
35.74	0.160	160.54	0.687
38.79	0.171	164.66	0.701
46.53	0.206	165.20	0.704
48.18	0.204	168.44	0.721
51.53	0.227	172.61	0.734
56.63	0.254	173.15	0.737
61.67	0.282	176.36	0.755
66.59	0.298	180.58	0.768
71.40	0.313	181.10	0.772
76.00	0.338	184.29	0.791
80.76	0.371	188.56	0.808
82.22	0.368	189.09	0.808
85.46	0.381	192.24	0.826
85.97	0.386	196.57	0.837
88.12	0.384	197.10	0.842
90.15	0.394	200.25	0.855
92.69	0.408	204.67	0.872
92.93	0.406	205.17	0.878
93.97	0.412	208.28	0.900
94.84	0.416	212.73	0.919
99.60	0.435	216.32	0.939
99.76	0.433	220.79	0.955
105.28	0.462	224.36	0.972
105.55	0.462	228.84	0.985
107.12	0.472	232.41	1.003
111.01	0.488	236.90	1.016
111.36	0.488	240.46	1.034
113.84	0.498	244.97	1.049
117.71	0.507	248.50	1.065
118.12	0.508	253.05	1.088
121.53	0.524	256.61	1.099
125.41	0.538	261.14	1.116
125.89	0.541	264.71	1.131
129.27	0.554	269.28	1.148
133.19	0.570	272.85	1.165
133.70	0.572	277.47	1.178
133.04	0.591	277.78	1.180
141.00	0.607	281.12	1.194
141.53	0.609	286.14	1.224
144.86	0.626	294.25	1.247
148.86	0.639	297.32	1.285
149.38	0.643	305.46	1.314
152.69	0.658	313.28	1.338
156.75	0.670	313.54	1.338

One of the aims of this investigation was to calculate the contribution of the guest species to the heat capacity and to compare this with C_p of the bulk guest species. As mentioned earlier, Dianin's compound and its adducts are particularly suited to this purpose because the empty host lattice exists and its heat capacity can be measured. By contrast, the β-quinol empty host lattice is unstable, but β-quinols are available at various guest occupancy levels [4, 13]. Unsolvated clathrate hydrates are unstable, and furthermore, the adducts occur only at fixed guest compositions [14]. Another particularly important feature of the adducts of Dianin's compound is that there is a relatively narrow range of unit cell parameters amongst the Dianin inclusion compounds, compared to, for example, β-quinol, indicating rigidity of the Dianin host lattice [4].

In order to calculate the heat capacity of the guest species (CCl_4) or guest dimer (ethanol), we have assumed the heat capacities of the guest(s) and the unsolvated host to be additive. Although this may be too simplistic, the relatively large cage of the Dianin's compound, the rigidity of the host lattice and the relatively weak guest–host interactions work in favour of this assumption. We have taken the stoichiometries of the ethanol adduct to be exactly 3 : 1, and that of the CCl_4 adduct to be 6 : 1, and calculated the molar heat capacities of the guest species. We note that the very similar heat capacities per gram for the adducts and the unsolvated Dianin's compound make the guest heat capacity rather insensitive to the occupancy of the cage, and therefore slight occupational deficiencies will not change our results significantly. We also note that the isochoric and isobaric heat capacities of the guest molecules will be the same if the guests are one per cage, and able to rotate freely [15]; in the ethanol adduct the first condition is not met, but both may be met in the CCl_4 adduct.

Figure 2 illustrates the single-molecule heat capacity of CCl_4 in the Dianin adduct as calculated from the experimental heat capacities of the unsolvated and CCl_4 adducts. The similarity between the single-molecule heat capacity and that of bulk CCl_4 (dashed curve) [15, 16] is striking, particularly in the region from about 60 K to 260 K. However, the single-molecule heat capacity differs from that of bulk CCl_4 in several ways, *viz.* there is a heat capacity plateau from about 100 K to 200 K, and there are no first-order phase transitions as observed in bulk CCl_4 [15]. The latter may reflect the decreased strength of orientational interactions in adjacent CCl_4 molecules in the clathrate; the average CCl_4 separation is 11 Å along the c-axis and 27 Å along the a-direction in the clathrate, compared with 5.8 Å in bulk CCl_4 [17, 18]. The source of the heat capacity plateau in the single-molecule heat capacity may be similar to that observed in the clathrate hydrate of tetrahydrofuran, i.e. fully-excited hindered rotational contributions [7]. It is known from the NQR study of the CCl_4 clathrate of Dianin's compound that the librational frequencies of the CCl_4 molecule are very low (37 and 47 cm^{-1}) [11], consistent with full thermal excitation (heat capacity plateau) above about 100 K. At lower temperatures, the single-molecule heat capacity is considerably less than that of bulk CCl_4, indicating, within the constraints of the assumption of additivity of the guest and host contributions to the heat capacity, that there are fewer low-frequency modes associated with CCl_4 in the clathrate relative to bulk CCl_4.

The molar heat capacity of the ethanol dimer, again calculated assuming additivity of the guest and host contributions, is illustrated in Figure 3. For comparison,

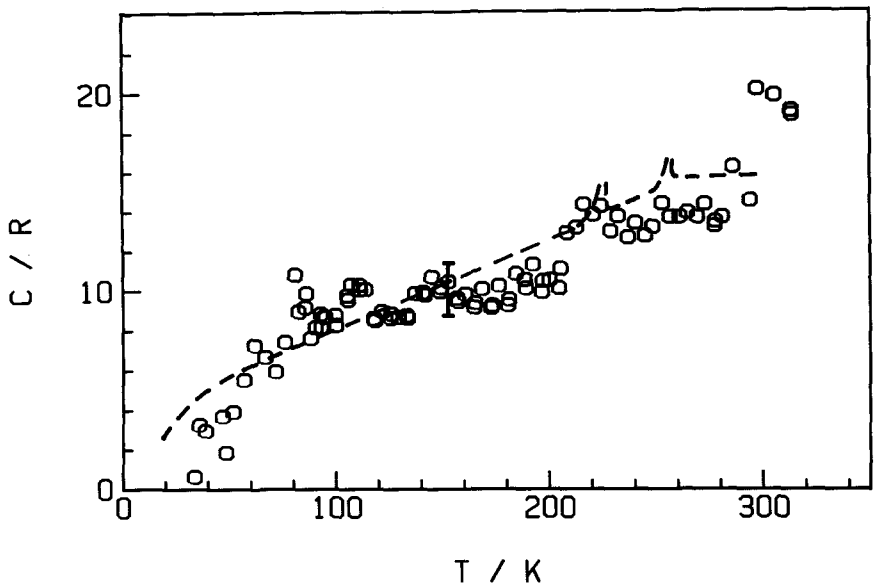

Fig. 2. The molar heat capacity of a CCl_4 molecule in the CCl_4 adduct of Dianin's compound. The dashed line indicates the molar heat capacity of bulk CCl_4 [15, 16], including its solid–solid transition at 226 K and its solid–liquid transition at 250 K. The error bar at $T = 150$ K represents the error in the molar heat capacity of the CCl_4 molecule in the clathrate, as propogated from an error of $\pm$ 0.5% in the heat capacity of unsolvated Dianin's compound and $\pm$ 0.5% in the CCl_4 adduct of Dianin's compound.

the heat capacity of bulk ethanol [19] is also illustrated (dashed curve). In contrast to the heat capacity of CCl_4, the heat capacity of the ethanol dimer differs considerably from the bulk solid. However, the match is closer above the melting point of pure ethanol. It appears that the heat capacity of the ethanol dimer is much more liquid-like than that of CCl_4 enclathrated in Dianin's compound. It is interesting to note here the properties of the tetrahydrofuran molecules in the tetrahydrofuran clathrate hydrate have been described as 'a glass in a crystalline matrix' [20]; the investigation of the degrees of freedom of the ethanol dimer in the ethanol adduct of **1** deserve further attention.

Based on the simple model of guest–host heat capacity additivity, the combined investigations of the CCl_4 and ethanol adducts allow us to conclude that the number of guest molecules in the cage does not determine whether or not the properties of the guest(s) are bulk-like: the single CCl_4 is more like the bulk than is the ethanol dimer. It would be of interest to see whether placement of a second CCl_4 molecule in the cage (in the thiol analogue of **1**) changes this result.

Further detailed investigations of clathrates of Dianin's compound could advance our understanding of this and other clathrates, but much remains unknown at this time. For example, it is possible, in principle, to calculate the contributions of the heat capacity of the guest molecules in the clathrate for comparison with Figures 2 and 3. Although one could estimate the contributions of the intramolecular vibrations, investigations of the dynamics of the guest(s) within the cage are

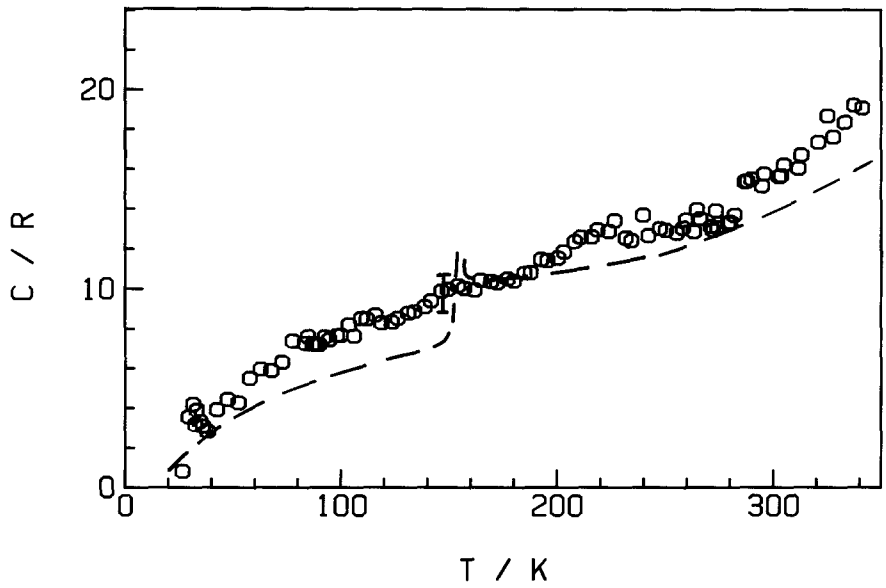

Fig. 3. The molar heat capacity of an ethanol molecule in the ethanol adduct of Dianin's compound. The dashed line indicates the molar heat capacity of bulk ethanol [18], including its solid–liquid transition at $T = 158.5$ K. The error bar at $T = 150$ K represents the error in the molar heat capacity of the ethanol molecule in the clathrate, as propogated from an error of $\pm$ 0.5% in the heat capacity of unsolvated Dianin's compound and $\pm$ 0.5% in the ethanol adduct of Dianin's compound.

required to allow calculation of the hindered-rotational and vibrational-rattling contributions of the guest heat capacity. For the purposes of comparison with other clathrates and theories of clathrate formation, another important area of investigation would be the experimental determination of the thermodynamic stability of unsolvated **1** as the host lattice. We hope that our outline of the relative simplicity of the Dianin system will provoke further investigations of these compounds.

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