

Heat Capacities of β -modification Phthalocyanines from 4 to 45 K

Anomalous Behaviour in Copper(II) and Nickel(II) Phthalocyanine

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Heat capacities from *ca.* 4 to *ca.* 45 K are reported for β -modification metal-free, copper(II) and nickel(II) phthalocyanine (β -H₂Pc, β -CuPc and β -NiPc where Pc = C₃₂H₁₆N₈).

β -CuPc undergoes two essentially first-order transitions implying the existence of three distinct phases, phase III stable below *ca.* 9 K, phase II stable from *ca.* 9 to *ca.* 12 K and phase I stable above *ca.* 12 K. Moreover, the sum of the two entropies of transition (for III \rightarrow II and II \rightarrow I) is so large (*ca.* $R \ln 4$, possibly more) that it is very likely that phase I is disordered in some way. To explain the value $R \ln 4$, we tentatively propose (i) that the disorder in phase I is positional disorder of the Cu²⁺ ions, to each of which there are presumed to be available four nearly equivalent potential minima in the central area of the Pc²⁻ ligand, and (ii) that in phase III the Cu²⁺ ions are ordered under the influence of their mutual interaction.

At temperatures between 4 and 8 K, the molar heat capacity of β -NiPc considerably exceeds those of β -H₂Pc and β -CuPc, and the latter heat capacities, unlike the former, are proportional to T^3 . This suggests that the heat capacity of β -NiPc below 8 K differs from those of β -H₂Pc and β -CuPc in including a substantial non-vibrational contribution.

The present study is concerned with three of the best-known phthalocyanine materials, namely β -modification metal-free, copper(II) and nickel(II) phthalocyanine. These are molecular crystals containing, respectively, the molecules H₂Pc, CuPc and NiPc (Pc = C₃₂H₁₆N₈), as depicted in fig. 1. All the atoms of the molecule lie approximately in a single plane. In the β -modification the molecular symmetry is found to be $\bar{1}$. The four central N atoms therefore define a parallelogram. The symmetry is, however, not far from being $4/mmm$, so that this parallelogram is almost a square.

Other polymorphs of the three compounds are known, but the β -modifications are the most stable and the best characterised. Moreover, there is an extremely close structural similarity between the three β -modifications (and also, incidentally, between these and the β -modifications of other phthalocyanines).¹⁻⁵ The respective phthalocyanine molecules are stacked in a very similar manner in each case. All three crystals have the space group $P2_1/a$ and the parameters of the (monoclinic) unit cells differ only slightly from one another.

Although the literature on phthalocyanines is very extensive, there is apparently no report of the heat capacity of any phthalocyanine at temperatures below 45 K. Our study was carried out to remedy this deficiency in respect of β -H₂Pc, β -CuPc and β -NiPc, and in the event it revealed several unusual and quite unexpected heat capacity features.

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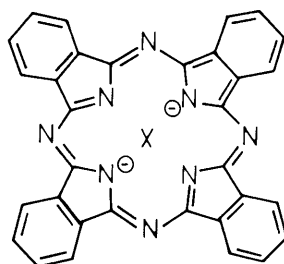


FIG. 1.—Structural formulae for the molecules H_2Pc , $CuPc$ and $NiPc$. X symbolises the metal ion (Cu^{2+} or Ni^{2+}) or two protons, but it should not be taken necessarily to indicate their precise position. The positions of the double bonds and the degree of ionic bonding are arbitrary; no single valence bond structure is satisfactory.

EXPERIMENTAL

PREPARATION AND CHARACTERISATION OF SAMPLES

ICI Ltd kindly supplied a laboratory-prepared sample of H_2Pc , in the form of a deep blue dust which analysed satisfactorily (% C, N, H = 74.6, 21.9, 3.5 observed; 74.70, 21.78, 3.53 calculated for $C_{32}H_{18}N_8$). However, its X-ray powder diffraction pattern (Debye-Scherrer) did not agree with that previously reported⁶ for β - H_2Pc . The material was presumed to be a less stable modification and was heated *in vacuo* to convert it into the β -modification (cf. literature reports^{6,7} of the irreversible conversion of α - H_2Pc to β - H_2Pc at *ca.* 200 °C). For this heat treatment the material was placed in an alumina boat in a silica furnace tube. The tube was connected to the pump initially and then periodically during warm-up. When the temperature outside the tube adjacent to the sample reached 310–385 °C, the tube was finally isolated from the pump and the temperature was maintained for over 4 h. Under these conditions only *ca.* 5% of the sample was lost by sublimation to cooler parts of the tube.

The product comprised lustrous small deep blue particles. Its powder diffraction pattern agreed with that previously reported⁶ for β - H_2Pc and could be indexed on the unit cell determined by single-crystal work.^{1,2} The analysis was practically unchanged by the heat treatment (% C, N, H = 74.5, 21.9, 3.6).

ICI also supplied laboratory-prepared samples of $CuPc$ and $NiPc$. The former analysed as 10.6% Cu by the KI/ $Na_2S_2O_3$ method (calculated for $CuC_{32}H_{16}N_8$: 11.03); the latter analysed as 10.1% Ni by the EDTA/pyrogallol-red method (calculated for $NiC_{32}H_{16}N_8$: 10.28). The $CuPc$ sample was a deep blue powder, whereas the $NiPc$ sample comprised lustrous small deep purple crystals which appeared to have been formed by sublimation. The infrared spectra of the materials (determined in nujol mulls) agreed with those reported⁸ for the respective β -modifications. The samples were then loaded into the calorimeter without further treatment. Inspection of powder diffraction photographs of the materials *ex calorimeter* confirmed that they were β -modification.

HEAT CAPACITY MEASUREMENTS

Two calorimeters were used. β - H_2Pc was run in "calorimeter B" described elsewhere,⁹ while β - $CuPc$ and β - $NiPc$ were run in the predecessor¹⁰ of calorimeter B. The two calorimeters used precisely the same germanium resistance thermometer for measurement of the sample temperature. Both were operated by the method of intermittent electrical heating.

The calorimetric samples comprised, respectively, 0.016 95 mol β - H_2Pc , 0.025 76 mol β - $CuPc$ and 0.019 64 mol β - $NiPc$. The gas used in the sample-containing vessel was ³He for β - H_2Pc and ⁴He for β - $CuPc$ and β - $NiPc$. All the results for β - H_2Pc were obtained in a single continuous run; for each of β - $CuPc$ and β - $NiPc$ the results above *ca.* 20 K were

obtained first and the results below *ca.* 20 K were obtained later in two or three consecutive runs.

RESULTS

The calorimetric results are presented in tables 1–3 and fig. 2 and 3. For β -H₂Pc from 4.5 to 18 K the fraction of the total measured heat capacity which was due to the sample was at least 50%, but above 18 K it diminished monotonically to 33% at 45 K. The corresponding fractions for β -CuPc and β -NiPc were greater

TABLE 1.—MOLAR HEAT CAPACITY OF β -H₂Pc

T_{mid}/K	$\Delta T/\text{K}$	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$	T_{mid}/K	$\Delta T/\text{K}$	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$
4.538	0.486	0.691 ^a	19.932	2.152	24.19
5.065	0.713	0.933 ^a	22.298	2.762	28.84
5.798	0.993	1.494 ^a	24.597	2.129	33.86
6.994	0.845	2.587 ^a	27.145	2.968	38.94
7.986	1.261	3.837 ^a	29.830	2.416	45.21
9.288	1.463	5.444	32.435	2.803	51.33
10.792	1.681	7.881	35.309	2.945	58.21
12.364	1.578	10.98	38.244	2.926	65.37
13.860	1.562	13.59	41.258	3.101	71.72
15.672	2.306	15.64	44.553	3.488	81.04
17.849	2.103	19.95			

^a Long equilibrium times (see text).

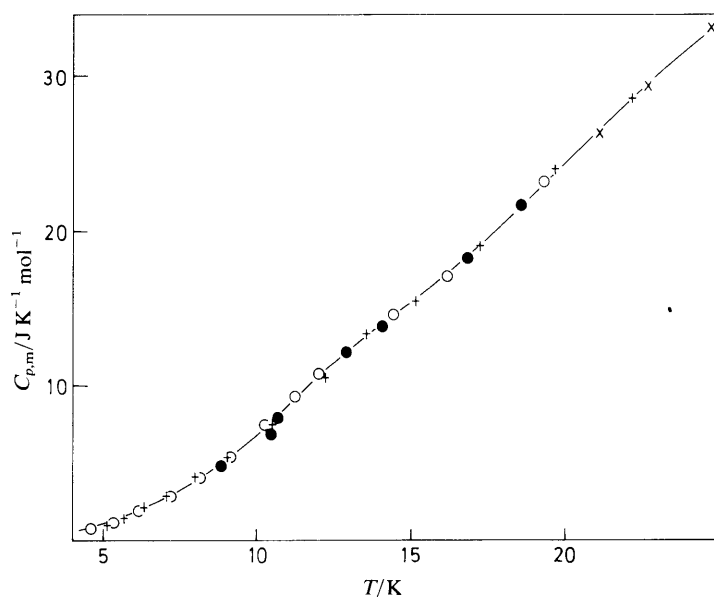


FIG. 2.—Molar heat capacity $C_{p,m}$ of β -CuPc below 25 K plotted against temperature T . The crosses (+), open circles (O) and filled circles (●) represent the values obtained in the first, second and third low-temperature runs, respectively. The crosses (×) are results obtained in a previous run which started at higher temperature. The first-order transitions are not shown.

TABLE 2.—MOLAR HEAT CAPACITY OF β -CuPc

T_{mid}/K	$\Delta T/\text{K}$	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$	T_{mid}/K	$\Delta T/\text{K}$	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$
>20 K run			second <20 K run		
21.12	1.387	26.32	4.66	0.443	0.841
22.66	1.697	29.20	5.30	0.977	1.276
24.70	2.397	33.26	6.18	1.117	1.974
26.92	2.048	37.99	7.19	1.522	2.954
29.48	3.063	43.51	8.13	1.094	4.154
32.51	2.998	50.00	9.20	1.781	5.52
35.59	3.189	56.82	10.27	1.313	7.57
38.82	3.259	63.81	11.21	1.562	9.37
42.57	4.245	71.25	*	*	*
46.79	4.202	80.83	12.00	2.334	10.88
first <20 K run			14.37	2.611	14.73
			*	*	*
5.13	0.573	1.125	16.10	3.513	17.15
5.67	0.660	1.498	19.26	2.868	23.26
6.29	0.761	2.096	third <20 K run		
7.06	0.908	2.937	8.85	2.036	5.02
8.00	1.107	4.171	10.44	1.779	6.99
9.15	1.384	5.519	*	*	*
10.54	1.597	7.740	10.62	2.820	8.03
12.12	1.692	10.71	12.86	1.819	12.26
13.56	1.327	13.43	*	*	*
15.10	1.873	15.52	14.03	2.874	13.97
17.19	2.394	19.16	16.77	2.748	18.37
19.62	2.568	24.02	18.55	0.938	21.76
22.15	2.619	28.58			

* * * indicates "events" described in text.

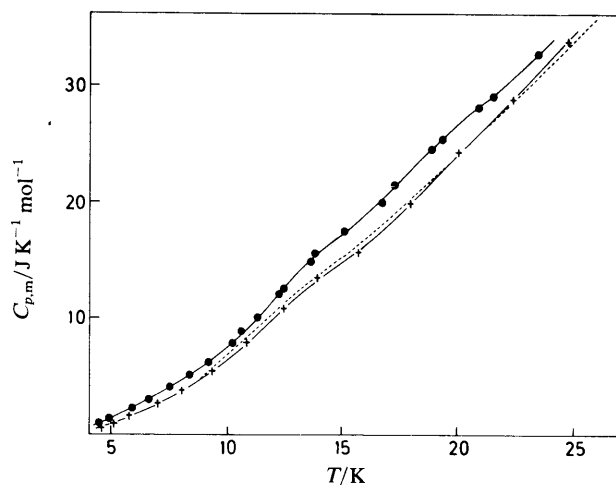


FIG. 3.—Molar heat capacity $C_{p,m}$ below 25 K plotted against temperature T for β -H₂Pc (+) and β -NiPc (●). The dotted curve, included for comparison, is identical with the curve shown in fig. 2 for β -CuPc.

TABLE 3.—MOLAR HEAT CAPACITY OF β -NiPc

T_{mid}/K	$\Delta T/\text{K}$	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$	T_{mid}/K	$\Delta T/\text{K}$	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$
>20 K run			11.26	1.308	10.13
			12.37	1.209	12.76
21.35	1.908	29.16	13.75	1.694	15.69
23.21	1.813	32.55	15.38	1.676	17.74
25.08	1.925	36.40	17.21	2.103	21.51
27.04	2.009	40.46	19.24	2.059	25.61
29.64	3.189	45.98	21.33	2.265	29.33
32.84	3.213	52.80	second <20 K run		
35.95	3.001	59.60			
38.89	2.872	65.56			
42.29	3.915	71.96			
46.19	3.894	81.09			
first <20 K run			4.75	1.027	1.276
			5.76	1.118	2.184
			6.74	1.046	3.301
4.49	0.446	1.029	7.86	1.454	4.81
4.91	0.450	1.351	9.13	1.409	6.28
5.36	0.584	1.753	10.53	1.725	9.12
5.90	0.663	2.259	12.14	1.718	12.22
6.60	0.949	3.134	13.62	1.399	15.15
7.47	0.979	4.088	14.99	1.484	17.20
8.31	1.013	5.15	16.73	2.169	20.13
9.18	1.044	6.19	18.73	2.003	24.69
10.15	1.214	7.87	29.73	2.158	28.12

because of the larger amounts of sample used. Curvature corrections were negligible.

In the measurements on β -H₂Pc between 4.5 and 9 K, relatively long times were needed before thermal equilibrium was established (>15 min after the end of the heating period). The $C_{p,m}$ in this range, however, were not abnormal. It is very unlikely that this slow approach to equilibrium was associated with adsorption of the ³He exchange gas in the sample vessel, since this gives rise to thermal effects only at much lower temperatures (<ca. 2.6 K).^{9,11}

With β -CuPc, altogether more remarkable behaviour was encountered in the <20 K range, where three separate heat capacity runs were performed. In the second and third of these, but not in the first, the following event took place twice in each run. When the sample, initially at temperature T_i , was electrically heated, its temperature rose at first but then began to fall, equilibrium being attained (ca. 15–30 min after the cessation of heating) at a final temperature T_f which was lower than T_i . The details are as follows (ΔH_m being the measured molar enthalpy change):

2nd <20 K run, 1st event: $T_i = 11.283 \text{ K}$, $T_f = 11.045 \text{ K}$, $\Delta H_m = 26.8 \text{ J mol}^{-1}$

2nd <20 K run, 2nd event: $T_i = 15.473 \text{ K}$, $T_f = 14.542 \text{ K}$, $\Delta H_m = 74.1 \text{ J mol}^{-1}$

3rd <20 K run, 1st event: $T_i = 10.621 \text{ K}$, $T_f = 9.326 \text{ K}$, $\Delta H_m = 28.6 \text{ J mol}^{-1}$

3rd <20 K run, 2nd event: $T_i = 13.634 \text{ K}$, $T_f = 12.692 \text{ K}$, $\Delta H_m = 80.1 \text{ J mol}^{-1}$.

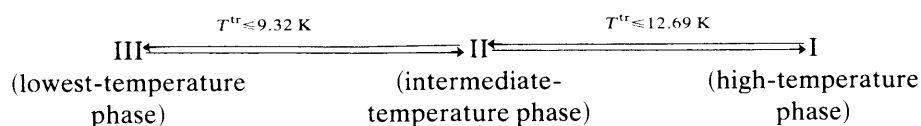
We will consider the possible interpretation of these results in the next section, but it is convenient to note two points here. First, there was no indication that these "events" resulted from any malfunction of the apparatus. Secondly, the $C_{p,m}$

calculated for all the determinations other than these four, including those of the first run, lie on one continuous curve (see fig. 2).

DISCUSSION

Each of the four "events" with β -CuPc indicates the occurrence of a transition in a sample which at the beginning of the determination was in a superheated low-temperature form. In such a case the heat input triggers the endothermic conversion to the stable high-temperature form and this can (depending on the total size of the heat input) lead to a net cooling. There is nothing fundamentally novel in this: similar observations could be made, for instance, on sulphur near 369 K (the rhombic-monoclinic transition temperature).

To explain the results on β -CuPc we find it necessary to assume that it can undergo *two* phase transitions implying the existence of three distinct phases whose ranges of thermodynamic stability are as follows:



(Note that the above notation I, II, III is provisional; according to convention, I is the solid phase stable immediately below the melting or decomposition temperature, so that a definitive naming of the present phases awaits an exhaustive search for phase transitions above the range of our own studies.)

We consider that in the cool-down prior to the first run the sample was supercooled in phase I and that it was for this reason that no phase transitions were observed on heating. Further, we consider that in the cool-down prior to the second and third runs, the conversions $I \rightarrow II \rightarrow III$ occurred at least partially, so that the reverse conversions were observed on heating. We believe both transitions to be essentially first order, since both are subject to supercooling and superheating and since neither is preceded by any abnormal rise in $C_{p,m}$.

The values given above as upper limits for the $III \leftrightarrow II$ and the $II \leftrightarrow I$ transition temperatures (9.32 and 12.69 K, respectively) are simply the T_f for the first and second "events" in the third run, on the basis that the cooling caused by the conversion of a superheated form into a low-temperature form cannot take the sample temperature below the equilibrium transition temperature. (Because the T_f of the second run were respectively higher than those in the third, they add nothing to our knowledge of the transition temperatures.)

The fact that the $C_{p,m}$ of all three runs lie on a single curve indicates that phases I, II and III have practically the same heat capacity in the temperature region of the transitions. It follows that the molar enthalpies of transition $\Delta H_m^{\text{tr}}(III \rightarrow II)$ and $\Delta H_m^{\text{tr}}(II \rightarrow I)$ are independent of temperature, which simplifies the following calculation of these enthalpies.

If one supposes that in the cool-down prior to the third run all of the sample was converted into phase III, then $\Delta H_m^{\text{tr}}(III \rightarrow II)$ and $\Delta H_m^{\text{tr}}(II \rightarrow I)$ are related to T_i , T_f and ΔH_m for, respectively, the first and second "events" in that run by the equation

$$\Delta H_m^{\text{tr}} = \Delta H_m + C'_{p,m}(T_i - T_f)$$

where $C'_{p,m}$ is the value of $C_{p,m}$ for $T = (T_i + T_f)/2$ indicated by the curve in fig. 2. Using the values given in the last section, we obtain $\Delta H_m^{\text{tr}}(\text{III} \rightarrow \text{II}) = 37.6 \text{ J mol}^{-1}$ and $\Delta H_m^{\text{tr}}(\text{II} \rightarrow \text{I}) = 92.1 \text{ J mol}^{-1}$. If one performs the same calculation with the values from the second run, the molar enthalpies of transition obtained are lower (29.0 and 88.6 J mol^{-1}), which indicates that in the cool-down prior to the second run the conversion to phase I was less complete than in the third. The pattern which now emerges, of the "sluggishness" of the phase transitions diminishing with thermal recycling, is a familiar one. In principle, the conversion to phase I may not have been quite complete even prior to the third run, so that the ΔH_m^{tr} calculated from it above may be underestimates.

In summary, $T^{\text{tr}} \leq 9.32 \text{ K}$ and $\Delta H_m^{\text{tr}} \geq 37.6 \text{ J mol}^{-1}$ for the $\text{III} \leftrightarrow \text{II}$ transition, and $T^{\text{tr}} \leq 12.69 \text{ K}$ and $\Delta H_m^{\text{tr}} \geq 92.1 \text{ J mol}^{-1}$ for the $\text{II} \leftrightarrow \text{I}$ transition. The corresponding entropies of transition are therefore ≥ 4.03 and $\geq 7.26 \text{ J K}^{-1} \text{ mol}^{-1}$. The sum of these figures is $11.29 \text{ J K}^{-1} \text{ mol}^{-1}$, which is nearly $R \ln 4$ ($\equiv 11.52 \text{ J K}^{-1} \text{ mol}^{-1}$). It is important now to note that even at much higher temperatures (up to 300 K and beyond) entropies of transition in solids as large as these are usually predominantly configurational in origin,^{12,13} *i.e.* the vibrational contribution usually amounts to only a minor part of the total, and that at 0 K any entropy difference between two forms of a solid must necessarily be entirely configurational in origin. The temperature of the present transitions being relatively near to 0 K, it seems justifiable to regard the observed entropy changes as almost entirely configurational in origin.

We must now consider what type of configurational disorder is being gained in the transitions. *A priori*, three types of disorder are worthy of consideration: magnetic, orientational and positional. The first of these can be ruled out for two reasons: (a) the maximum magnetic entropy which a mole of β -CuPc could gain would be $R \ln 2$ (since the Cu^{2+} ion has only one unpaired electron), only one-half of the total entropy gain in the two transitions, and (b) recent magnetic susceptibility measurements¹⁴ in fields of 20–1400 Oe have indicated that β -CuPc is magnetically disordered even at 4.2 K, well below the temperature of the transitions under consideration. Orientational disordering at such low temperatures as this is rare, and apparently confined to small hydride species (*e.g.* H_2 , CH_4 and $-\text{NH}_3$);¹³ it seems highly improbable that a rigid molecule as large as CuPc could undergo the necessary fourfold disordering at 9–12 K, as the activation energy would be too high compared with kT . So we are led to consider the possibility that positional disorder is involved, of a kind in which the movement from one possible position to another is impeded only by a very low potential barrier.

Prompted by the value $R \ln 4$ and by the approximate fourfold symmetry of the CuPc molecule, and pending diffraction studies on β -CuPc at liquid-helium temperatures, we tentatively suggest that the transitions may involve fourfold positional disordering of the Cu^{2+} ions in the plane of the molecule. This can arise if the potential energy of the Cu^{2+} ion is not a minimum for the position in the centre of the molecule, but a maximum (such a possibility being quite conceivable, especially in view of the rigidity of the ligand). If such is the case, then the approximate $4/mmm$ symmetry requires that there should be four potential energy minima surrounding the maximum, as is shown schematically in fig. 4. Fig. 4 is not based on calculation; the potential energy contours are at arbitrary intervals and the ratio of the distance between adjacent minima to that between adjacent N atoms has been chosen arbitrarily. Also, it is possible that all the potential minima should be rotated through 45° about the centre. None of these *caveats* detract from the validity of the proposition that if there is a potential maximum in

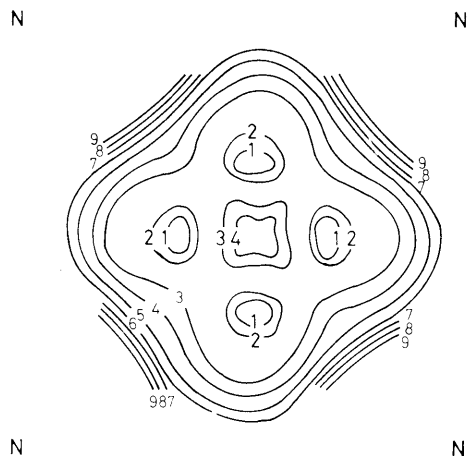


FIG. 4.—Potential energy function (not quantitative and not to scale) which would be consistent with fourfold disordering of the Cu^{2+} ions at sufficiently high temperatures. 1, 2, 3 . . . 9 are contour lines of increasing potential energy of the Cu^{2+} ion in the plane of the four central N atoms.

the centre of the molecule then there will be four minima positioned at the corners of a square having its centre coincident with that of the molecule. (The possibility of there being 8, 12, 16, *etc.* minima, although permitted by the symmetry, can in our view be reasonably ignored, for physical reasons.)

In phase I immediately above the upper T^{tr} , we envisage each Cu^{2+} ion as spending most of its time vibrating in one of the four potential minima, only occasionally crossing between minima, the probability that any ion will be in a particular minimum of the four available to it being $1/4$. When the crystal is cooled sufficiently the forces tending to order the ions relatively to one another become significant and such ordering will actually occur, so long as the cooling is slow enough to permit the necessary crossing of potential barriers between minima. We envisage that in phase III such ordering is complete and that there is long-range correlation between the positions of the Cu^{2+} ions.

Since the conversion between phases I and III is capable of taking place below 12.69 K, the barriers cannot be large compared with kT at this temperature. This makes it likely that the size of the square formed by the minima is small compared with that formed by the N atoms and indeed that (referring to fig. 4 for the sake of definiteness) that the area enclosed by, say, contour 5 is also small. This has importance for room-temperature X-ray diffraction experiments on phase I. At room temperature, kT may well be so large compared with the difference in energies between contours 1 and 5 that the motion of the Cu^{2+} ion will essentially be vibration about the central position, such vibration not noticeably differing in amplitude or anisotropy from what one would consider reasonable for a simple potential function with a central minimum. Therefore, the fact that X-ray crystallographers^{1,4} have described the room-temperature structure as one in which Cu is positioned centrally does not preclude the above hypothesis. Moreover, a further phase transition in β -CuPc has been reported¹⁵ to occur at 10 °C, so that the room-temperature phase may in fact differ from our phase I in any case.

Evidently, on the above basis phase II must be one in which the Cu^{2+} ions are partly ordered. We offer no detailed suggestions as to the nature of this partial

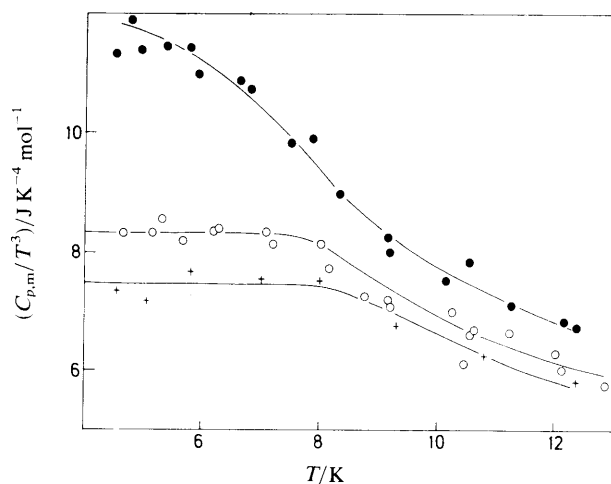


FIG. 5.—Test of the Debye T^3 law for β -H₂Pc (+), β -CuPc (○) and β -NiPc (●).

ordering. However, it is of interest that the change from the fully ordered phase III to the fully disordered phase I should occur stepwise. Double heat capacity maxima have been observed before⁹ in cases where (like this) the species undergoing ordering are arranged in chains in the crystal.

We turn now to a comparison of the heat capacities of β -H₂Pc, β -CuPc and β -NiPc at the lower end of the temperature range studied, where an approach to the Debye T^3 law might be expected for a purely vibrational heat capacity. Fig. 5 displays $C_{p,m}/T^3$ for the determinations below 13 K.

The heat capacities of β -H₂Pc and β -CuPc appear to obey the T^3 law below ca. 8 K with $C_{p,m}/T^3 \approx 7.5$ and $8.3 \text{ J K}^{-4} \text{ mol}^{-1}$, respectively. Therefore it is reasonable to suppose that both heat capacities are primarily vibrational below 8 K.

One would expect that if the heat capacity of β -NiPc were also primarily vibrational, then it should be very similar to that of β -CuPc because of the similarity of the masses of Ni and Cu. In fact, it is higher over the entire 4–45 K range and below 8 K the difference is proportionately very large, with $C_{p,m}/T^3$ continuing to rise with decreasing T . This suggests that the heat capacity of β -PcNi includes a substantial non-vibrational contribution at least up to 8 K. We cannot positively identify the nature of such a contribution. However, one can eliminate the possibility that what we have observed below 8 K is the "tail" of a magnetic or Schottky¹⁶ heat capacity anomaly, because even at 300 K the magnetic properties¹⁷ of β -NiPc are consistent with the practically exclusive population of the singlet (diamagnetic) ground state of the molecule (corresponding to the zero-spin d^8 configuration of the Ni²⁺ ion known also in other square planar Ni²⁺ complexes).

The results reported in this paper are complex, both β -CuPc and β -NiPc behaving unexpectedly at low temperatures, although in different ways. Our present explanation of the behaviour of the former is speculative and of the latter incomplete. Other observations of thermodynamic significance have been made in recent years: β -H₂Pc, β -CuPc and β -NiPc have all been reported to undergo phase transitions near room temperature,^{7,15} while neutron diffraction on β -H₂Pc has indicated⁵ that the two central H atoms of β -H₂Pc at room temperature are disordered among four positions within the (approximate) square defined by the

four central N atoms. It appears that further heat capacity measurements on the three materials are needed, if a comprehensive explanation of these earlier results and of the present results is to be achieved. On the one hand, measurements below 4 K should help identify the nature of the non-vibrational contribution to the heat capacity of β -NiPc; on the other, measurements from 45 to 300 K would enable one better to relate the heat capacity results at <45 K to the room-temperature crystal structure determination. Preferably, the measurements on each of the three materials should be performed with the same batch of fairly large sublimed crystals, so as to minimise any differences in behaviour due to particle size and thermal history.^{18,19}

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- ¹ J. M. Robertson, *J. Chem. Soc.*, 1935, 615.
- ² J. M. Robertson, *J. Chem. Soc.*, 1936, 1195.
- ³ J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219.
- ⁴ C. J. Brown, *J. Chem. Soc. (A)*, 1968, 2488.
- ⁵ B. F. Hoskins, S. A. Mason and J. C. B. White, *Chem. Commun.*, 1969, 554.
- ⁶ E. W. Karasek and J. C. Decius, *J. Am. Chem. Soc.*, 1952, **74**, 4716.
- ⁷ M. Füstöss-Wégner, *Thermochim. Acta*, 1978, **23**, 93.
- ⁸ A. A. Ebert and H. O. Gottlieb, *J. Am. Chem. Soc.*, 1952, **74**, 2806.
- ⁹ M. Jewess, S. Lee-Bechtold and L. A. K. Staveley, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 803.
- ¹⁰ R. M. Clay and L. A. K. Staveley, *Trans. Faraday Soc.*, 1966, **62**, 3065.
- ¹¹ P. Bloembergen and A. R. Miedema, *Physica*, 1974, **75**, 205.
- ¹² D. M. Newns and L. A. K. Staveley, *Chem. Rev.*, 1966, **66**, 267.
- ¹³ N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Oxford University Press, Oxford, 1978).
- ¹⁴ A. K. Gregson, personal communication.
- ¹⁵ B. Dudreva and S. Grande, *Ferroelectrics*, 1974, **8**, 407.
- ¹⁶ H. M. Rosenberg, *Low-Temperature Solid State Physics* (Oxford University Press, Oxford, 1963), chap. 3, pp. 23–30.
- ¹⁷ C. G. Barraclough, R. L. Martin and S. Mitra, *J. Chem. Phys.*, 1971, **55**, 1426.
- ¹⁸ R. E. Gerkin and K. S. Pitzer, *J. Am. Chem. Soc.*, 1962, **84**, 2662.
- ¹⁹ L. V. Gregor and K. S. Pitzer, *J. Am. Chem. Soc.*, 1962, **84**, 2664.