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PHASE TRANSITIONS IN LAYER-INTERCALATION COMPOUNDS OF NICKEL CYANIDE WITH *n*-ALKYLAMINES

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Résumé. — On met en évidence l'existence de deux étapes dans la désorganisation par chauffage du système de chaînes paraffiniques intercalées entre les couches tétracyanonickélate de Ni du composé cyanure de Ni-*n* dodécylamine. Les spectres IR et de diffraction X subissent d'importantes modifications aux environs de 55 et de 90 °C, les enthalpies de transitions correspondantes (solide-solide et solide-liquide respectivement) étant approximativement dans le rapport 4 : 1. La série comportant des alkylamines normales en C_{*n*} est étudiée pour *n* = 12 à 16 : on montre l'influence sur la première transition de la parité du nombre d'atomes de carbone de la chaîne paraffinique.

Abstract. — A two step modification phenomenon is observed, upon heating, within the intercalated chain system of the nickel cyanide-*n* dodecylamine compound : strong modifications of both X-ray diffraction patterns and IR spectra take place at 55 and 90 °C. The enthalpy of the observed transitions (respectively solid-solid and solid-liquid) are roughly in the ratio 4 to 1. The study of *n* alkylamines compounds from dodecyl to hexadecylamine shows that the parity of the number of C atoms of the alkylamine chain has a significant effect on the first transition.

The ability of systems such as graphite [1], chalcogenides [2, 3], silicates [4, 5] to intercalate molecules within their layer lattices is well known. It is also known [6-10] that bonding of various molecules by their polar end-groups to the N-coordinated Ni atoms of nickel cyanide complexes leads to solid layer intercalation compounds showing definite interlayer spacing. By examining compounds with n from 2 to 18 at two or three temperatures Walker and Hawthorne [11] have pointed out the ability of n -alkylamine chains thus intercalated (Fig. 1) to demonstrate a liquid-like or crystal-like structural character.

By studying compounds from $n = 12$ to $n = 16$ in the temperature range $-120\text{ }^{\circ}\text{C}$ to $130\text{ }^{\circ}\text{C}$, we were able to find a solid-solid transition within the intercalated chain system, prior to the *melting* of the chains.

Preparations of form I (see below) of the Ni cya-

FIG. 1. — Proposed structure of an *n*-alkylamine nickel cyanide complex after Weiss 1958.

nide-*n* alkylamine compound in the 1 : 1 ratio for Ni(CN)₂/C_{*n*}H_{2*n*+1}NH₂ (*n* = 12 to 16) will be reported elsewhere [12].

Taking $n = 12$ as an example, the differential thermal analysis (DTA) shows, without any loss of mass, a remarkably simple thermogram consisting of two endotherms starting around 55 °C and 90 °C, thus defining the domains of three distinct forms (I, II, III) of the complex (Fig. 2A).

FIG. 2. — DTA thermograms : A : $C_{12}H_{25}NH_2$ compound ;
B : $C_{13}H_{27}NH_2$ compound.

The weaker signal, around 90° (transition II → III), is reversible on cooling regardless of the cooling rate. The recovery of form I on cooling can also be detected by DTA : the process takes hours in the range 30-50 °C, but is much faster at lower temperatures. Estimation of the enthalpies by peak-area measurement leads to values of 0.45 cal and 0.12 cal per methylene group of amine $C_{12}H_{25}NH_2$ respectively for transitions I → II and II → III; the same procedure leads to a value of 0.92 cal per CH_2 group for the melting of the pure amine.

The most striking change on heating from I is the progressive disappearance of the splitting of two infra-red bands which can be ascribed to intra-chains vibrations (Table I). Above 90 °C (form III) the only well defined bands can be ascribed to the nickel cyanide network vibrations.

TABLE I

	Room temperature (form I)	80 °C (form II)
CH_2 symmetric bending frequencies (cm^{-1})	1 465 + 1 475	1 465
CH_2 rocking frequencies (cm^{-1})	720 + 730	720

Table II gives X-ray powder diffraction data of form I ($n = 12$).

TABLE II

d obs (Å) at room temperature in form I
of $C_{12}NH_2$ -Ni cyanide compound

16.3 vs, sharp	4.20 vvs	2.42 w
9.56 vw	4.04 w	2.37 w
8.10 vs, sharp	3.67 s	2.30 w
7.16 m	3.21 w	2.20 w
6.72 vvw	3.09 w	2.15 w
6.39 vvw	2.74 w	2.09 w
5.40 s, sharp	2.66 w	1.85 w
5.02 s	2.51 m	1.72 w
4.83 s	2.49 w	1.67 w
4.32 w	2.47 w	1.62 w

Attempts to calculate a satisfactory unit cell were unsuccessful. The diffraction lines have different temperature evolutions :

1° Some (16.3, 8.10, 5.40...) are sharp and considerably enhanced when the samples are prepared by sedimentation from a liquid suspension; these can be ascribed to the successive orders of reflexion for the basal spacing from 16.2 to 18.0 Å at ~ 60 °C and from 18.0 to 19.0 Å at ~ 90 °C;

2° Some lines (7.16, 5.02...) remain practically unchanged, the corresponding values of the interplanar distances are those (already known) characteristic of Ni-Ni distances in the Ni cyanide planes;

3° The strongest line in form I, namely at 4.2 Å (a well known characteristic distance in the closed

packing of paraffin chains [13]) is no longer present in form II; in form III, only the lines referred to in 1° and 2° are present.

The II → III changes in the X-ray diffractogram are reversible on cooling between 110 and 70 °C, while changes corresponding to II → I between 80 °C and room temperature are more sluggish.

The increase of the basal spacing at the first transition temperature (~ 60 °C) can be related to an increase of the van der Waals repulsion envelopes of the chains (calculated chain length ~ 18.9 Å) : the disappearance of splitting in the IR spectrum suggests a loss of coupling between CH_3 and/or CH_2 groups of neighbouring chains. Prior to the second transition temperature (~ 90 °C), the thermograms suggest (Fig. 1A, line ab) that the number of accessible states (configurations) of the chain-molecules increases progressively and cooperatively until all these molecules (which are still regularly (viz., crystallographically) bonded to the Ni cyanide two-dimensional network), present no other crystal-like character. The approximate 4 : 1 ratio of the enthalpies (and roughly of the entropies) associated with the two successive transitions shows that the solid-solid (I → II) phase transition is a much more important step in disordering the crystal-like arrays of chains of polymorph I than the subsequent (II → III) transition or *melting* of the already disordered array within the interlayer space.

The following basal spacings d have been measured :

TABLE III

	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
Form I	16.2	17.1	18.0	18.9	19.7
d (Å) Form II	18.0		20.0		22.0
Form III	19.0		21.2		23.5

Table III shows a linear increase of d with n in the three forms. Assuming for the alkyl chains in form I a fully stretched configuration, this rate of increase leads to an angle of ~ 45°; using this value, the calculated basal spacing :

$$d_{\text{calc.}} = (Ni-N) + (N-C) \sin \alpha_1 + (n-1) \times \\ \times (C-C)^* \sin \alpha_1 + r_{CH_3} + \delta$$

where Ni-N : 2.1 Å [7],

$$N-C = 1.47 \cos \left(\frac{180 - 109.5^\circ}{2} \right)$$

$$(C-C)^* = 1.54 \cos \left(\frac{180 - 109.5^\circ}{2} \right),$$

$$r_{CH_3} = 2.0 \text{ Å (van der Waals radius of the } CH_3 \text{ group)}$$

and

$$\delta = \frac{1}{2} 3.2 \text{ Å} = \text{half thickness}$$

of the $Ni(CN)_2$ planes [14]

is in excellent agreement with d_1 observed.

The assumption of fully stretched alkyl chains in form II would similarly lead to $\alpha_{II} \sim 53^\circ$; however,

FIG. 3. — Transition and melting temperature : $\circ$ Melting of the pure amines $C_nH_{2n+1}NH_2$ $n = 12$ to 16 . $\odot$ In layer transition and melting of the amines in the corresponding Ni cyanides compounds.

X-rays and infra-red spectra do not fully support this assumption in the case of form II and certainly exclude it in the case of form III.

In figure 3, the transition and *melting* temperatures (defined as the beginning of the DTA signal) are given for the cyanide compounds with $n = 12$ to 16 ; they are always above the melting temperature of the corresponding pure n alkylamines. For the C_{13} and C_{15} compounds, the DTA thermograms show a splitting of the $I \rightarrow II$ endotherm, the relative intensity of the $A\alpha$ and $A\beta$ signals (Fig. 2B) depending on the thermal history. Moreover, upon cooling, these complexes revert back to form I much more easily than the *even* complexes. This versatile behaviour seems to be consistent with the Walker hypothesis [11] concerning the existence of two distinct conformations in the complexes with odd intercalates.

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