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PHASE TRANSITIONS OF CYANOMERCURATES

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SUMMARY

Quaternary Cyanomercurates $NR_4^+[MHg(CN)_4]^-$ with R=Et,Pr; M=Li,Na, K,Cu, obtained by reactions of NR_4CN, MCN and $Hg(CN)_2$ in polar solvents are dimorphous. The crystal structures of the two forms were determined by X-ray diffraction. The low temperature modifications are tetragonal with a space group $I\bar{4}$, the high temperature forms are cubic with the space group $F\bar{4}3m$. In both structures tetrahedral $M(NC)_4$-and $Hg(CN)_4$- groups are connected by M-CN-Hg bridges to a three dimensional framework of cristobalite type structure with cavaties, of which the NR_4^+ cations are located. Reversible phase transitions, which have been studied by DTA/DSC, X-ray diffraction, Raman and MAS-NMR spectroscopy, are of first order and of displacive character. They are related closely to transitions of other important compounds with a cristobalite type structure.

INTRODUCTION

The well-known structural analogy between oxo- and cyanocomplexes of the d^{10}-cations Cd(II) and Hg(II) prompted us to investigate ternary and quaternary cyanomercurates with large countercations (ref.1). On that occasion we obtained, by reactions of $Hg(CN)_2$ with NaCN and NEt_4CN, the cyanomercurate $NEt_4[NaHg(CN)_4]$ which shows a filled cristobalite-type structure. The cubic compound undergoes a rapid reversible phase transition at -34°C in a tetragonal low temperature form. This observation and the analogy of the structure to the alumosilicate carnegieit $NaAlSiO_4$ (ref.2) were the motivation of this study. In this paper we present the results of attempts to synthesize further compounds of this formula type and of investigations of the phase transitions by X-ray diffraction, spectroscopic methods and DTA/DSC.

EXPERIMENTAL RESULTS

Cyanomercurates, $NEt_4MHg(CN)_4$, with the cubic high-temperature form were obtained by reactions of NEt_4CN, MCN and $Hg(CN)_2$ in ethanol at room temperature with M=Li,Na and Cu. Reactions of NPr_4CN lead to corresponding compounds with M=Na,K, but they are related to the tetragonal low temperature modifications. From the quater-

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nary system $NEt_4CN/NPr_4CN/NaCN/Hg(CN)_2$ we obtained mixed crystals of $(NEt_4)_{1-x}(NPr_4)_xNaHg(CN)_4$ in the cubic form for $0<x<0.8$ and in the tetragonal low temperature form with $x>0.8$. All attempts failed to exchange M in the cubic modifications with Rb,Cs,Ag, and Tl and also the exchange of NR_4^+ with NMe_4^+ and NBu_4^+. Colourless, tetrahedrashaped crystals of $NEt_4MHg(CN)_4$ with M=Li,Na and $NPr_4MHg(CN)_4$ with M=Na,K were grown from dichlormethane/ethanol solvent mixtures. Single-crystal X-ray diffraction studies were made on Nonius CAD 4 diffractometer using Mo $K_\alpha$radiation and the structures were solved and refined by using the programs of Shelx 76 (ref.3). The phase transitions were studied on powder samples by X-ray diffraction (Guinier-Simon camera, Cu $K_\alpha$radiation, Fa.Nonius), ^{13}C- and ^{23}Na-MAS-NMR-spectroscopy (CXP 300, Fa. Brucker), Raman spectroscopy (U 1000, Fa.Jobin-Yvon, Ar-Laser) and DTA/DSC (Thermoanalyzer STA 429, DSC 444, Fa.Netzsch) at variable temperatures in the range from +200°C to -150°C. The results are given in Table I.

TABLE 1

Unit Cell Dimensions, Transition Temperatures and Thermochemical Data

	$NEt_4[MHg(CN)_4]$			$NPr_4MHg(CN)_4$	
	Li	Na	Cu	Na	K
a_{cub}(pm)	1211.2 (2)	1253.8	1211.2	1311.0	1319.0(3)
a_{tet}(pm)	818.17(2)			997.3(2)	999.5(2)
c_{tet}(pm)	1282.30(5)			1083.2(4)	1087.5(3)
T_{tr} (°C)	-50	-34	-58	165	167
$\Delta H(kJmol^{-1})$	1.72	2.70	1.15	6.68	5.30
$\Delta S(JK^{-1}mol^{-1})$	7.7	11.30	5.33	15.25	12.05

DESCRIPTION OF THE CRYSTAL STRUCTURES

The structures of both forms are equivalent in topology. In the crystal structures tetrahedral $Hg(CN)_4$ and $M(NC)_4$ fragments are bridged by Hg-CN-M-chains to a three dimensional framework. The corner-connected tetrahedra form adamantane-like cages of $Hg_6(CN)_{12}M_4$ and $Hg_4(CN)_{12}M_6$. Only the centres of the Hg_6M_4 cages are occupied by the NR_4-cations in the sense that the R-groups are pointing at the centres of the four $Hg_3(CN)_6M_3$ hexagons which are in the chair conformation (Fig.1).

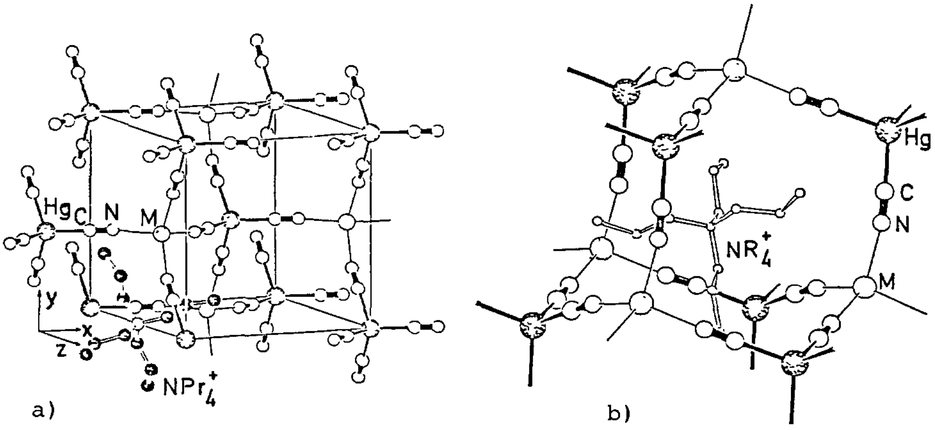

Fig.1. Network of the tetragonal lattice a) and the resulting adamantane-like cage b) centred by a R_4N^+-cation.

The tetrahedral fragments $Hg(CN)_4$, NR_4 and the M-cations occupy positions of the site symmetry T_d-$\bar{4}3m$ in the case of the cubic high-temperature modifications with the space group $F\bar{4}3m$. In the tetragonal low-temperature forms with the space group $I\bar{4}$, the site symmetry S_4-$\bar{4}$ is realized. The most important difference between the structural arrangements is found in the connections of the tetrahedra. The Hg-CN-M-bridges are linear in the cubic high-temperature forms, but nonlinear in the tetragonal low-temperature forms (Fig.2).

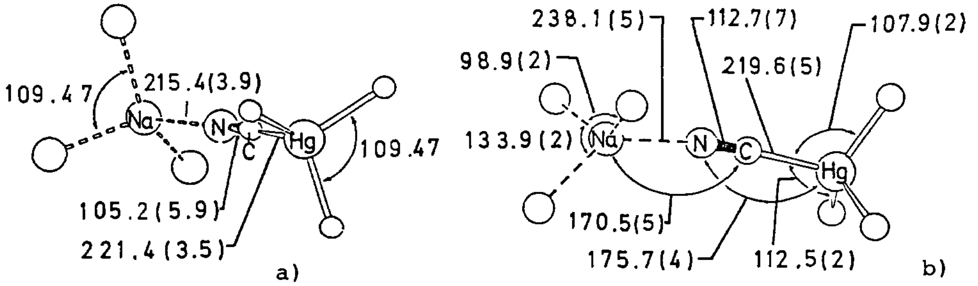

Fig.2. The Hg-CN-M-bridges a) in the cubic $[Et_4NNaHg(CN)_4]$ are linear and b) in the tetragonal $[Pr_4NNaHg(CN)_4]$ are angular (at 20°C).

The structural distortion is a result of contrarotating of the tetrahedra. Additionally the $M(NC)_4$ tetrahedra were found to be slightly distorted.

THE PHASE TRANSITIONS

All of the cubic cyanomercurates undergo rapid and reversible continuous phase transformations of first order. The spectroscopic results showed that the transitions are displacive, i.e. no bond is broken and no bond is added. As the result of distortion and rotating of the tetrahedral $Hg(CN)_4$- and $M(CN)_4$-groups a loss of symmetry take place (Scheme).

$$F\,\bar{4}\,3\,m,\ Z = 4 \xrightarrow{t(3)} I\,\bar{4}\,2\,m,\ Z = 2 \xrightarrow{t(2)} I\,\bar{4},\ Z = 2$$

The structures and the phase transitions are related closely to the high-temperature modifications of cristobalite (refs.4,5) $AlPO_4$ (ref.6) and $NaAlSiO_4$ (ref.2). In our opinion the quaternary cyanomercurates could be a model system for understanding the phase transitions of these important compounds.

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