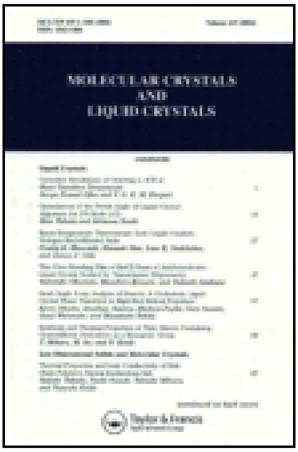

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New Organic Metals $ET_2[Hg(SCN)Cl_2]$ and $ET_2[Hg(SCN)_2Cl]$

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NEW ORGANIC METALS $ET_2[Hg(SCN)Cl_2]$ and $ET_2[Hg(SCN)_2Cl]$

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Abstract New two-dimensional organic metals $ET_2[Hg(SCN)_{3-n}X_n]$, X=F,Cl,Br,I have been synthesized and investigated. $ET_2[Hg(SCN)Cl_2]$(I) and $ET_2[Hg(SCN)_2Cl]$(II) are isostructural. Cationic sheets of ϰ-type alternate with anionic sheets. The anions $[Hg(SCN)_{3-n}Cl_n]^-$(n=1,2) have a polymeric structure and form the chains with one or two bridge ligand SCN. Both salts have a metallic character of conductivity till 35 K (I) and 50 K (II), respectively, at lower temperatures they become insulators.

Latest progress in the field of organic metals and superconductors based on bis(ethylenedithio)tetrathiafulvalene is connected with design and using of polymeric metal containing anions [1].

In the first organic superconductors with metal containing anions $ET_4(Hg_{3-\delta}X_8)$,X=Cl,Br [2-4],organic sheets consisted of ET dimers (ϰ-phase) alternate with anionic sheets constructed of Hg-containing polymeric chains. Later on a lot of superconductors with metal containing anions $[Cu(NCS)_2]^-$[5],$\{Cu[N(CN)_2]X\}^-$X=Cl,Br [6,7], $[NH_4Hg(SCN)_4]^-$,

[8], $[Ag(CN)_2H_2O]^-$ [9], $\{Cu[N(CN)_2]CN(H_2O)_n\}$ (n=0,1) [10], have been shown to have mainly the ϰ-phase structure of cationic sheet and complicated polymeric anions. Organic superconductors $ET_2[Cu(NCS)_2]$[5], $ET_2\{Cu[N(CN)]_2CN\}$ [10] and $ET_2\{Cu[N(CN)_2]X\}$ (X=Br,Cl) with the highest temperatures of superconducting transition being equal to 10.4, 10.7, 11.6 and 12.8 K (at 0.3 Kbar), respectively, have just these polymeric metal containing anions.

We have synthesized new organic metals $ET_2[Hg(SCN)_{3-n}X_n]$ X = F,Cl,Br,I with polymeric anions $[Hg(SCN_{3-n}X_n]$ [11]. Single crystals of $ET_2[Hg(SCN)Cl_2]$(I) and $ET_2[Hg(SCN)_2Cl]$ (II) were prepared by electrocrystallization of ET ($c=2,5\ 10^{-5}$M) with the mixture of $Hg(SCN)_2$, Me_4NSCN KCl and 18-crown-6 in 1:1:1 relation (c=0,01 M) in 1,1,2-trichloroethane and 10%(vol) ethanol solution with a constant current being equal to 1 μA. Synthesis was carried out at 40°C to yield (I) and at 20°C for (II). Black thin platelet crystals of distorted rhombic shape were harvested after a week in both cases.

The final stoichiometry was determined by crystal structure analyses [12]. The salts (I) and (II) are isostructural, parameters of their elementary units are close and equal to:

	$ET_2[Hg(SCN)Cl_2]$	$ET_2[Hg(SCN)_2Cl]$
a	36.642(11)A	36.69(1)A
b	8.300(4)A	8.302(8)A
c	11.798(1)A	11.732(8)A
β	89.91(3)	90.02(6)°
V	3588.1(9)A^3	3573.2(8)A^3
Sp.gr.	Cc	Cc
Z	4	4
d_{calc}	2.05 g/cm^3	2.08 g/cm^3
R	0.071	0.067

In the investigated compounds as well as in other ET salts, cationic sheets alternate with anionic ones along a-axis. Organic sheets of (I) and (II) consisted of ET dimers, have a packing pattern of ϰ-type (fig.1). Interplanar distances between ET molecules in the dimers are equal to 3.59 A and 3.53 A, respectively. ET radical-cations are mutually shifted on the length of central C=C bond. In (I) there are no shortened distances inside the dimer, in (II) one of the S...S distances is equal to 3.54 A. ET molecules from neighbouring dimers are connected by shortened S...S contacts in the range of 3.40 - 3.53 A (fig.2). Radical-cations form corrugated bands in the c-direction in such a manner, that one band contains only A radical-cations, while another band consists of only B radical-cations.

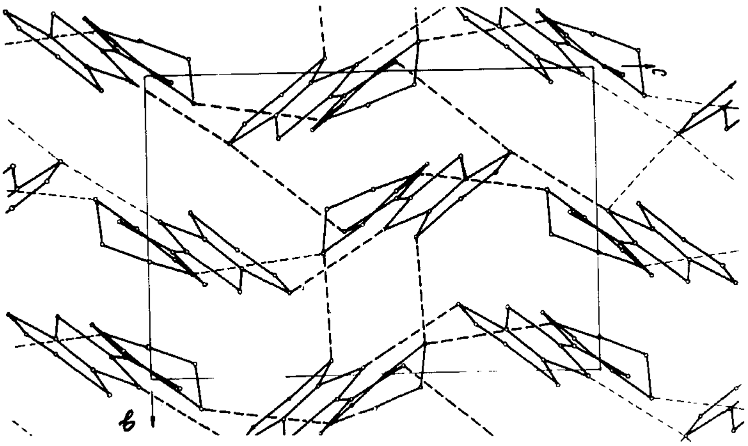


Fig.1. Packing of organic sheets in (I) and (II) (ϰ-phase).

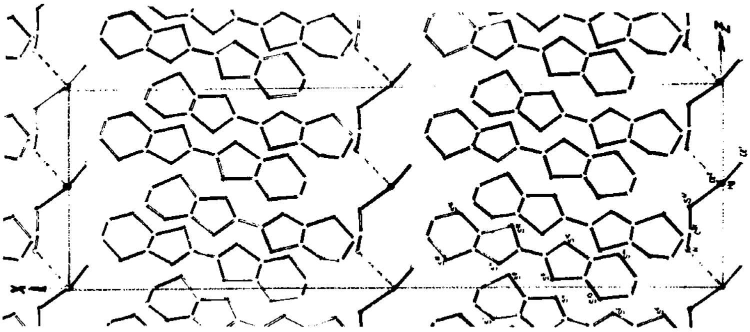
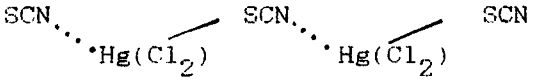
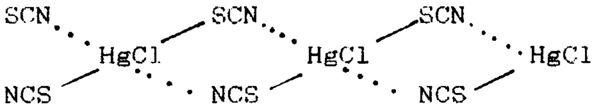


Fig.2. View of cationic and anionic sheets in (I).

Bidentate character of the -SCN-ligand leads to the formation of polymeric anion so the anionic sheets of both compounds contain repeated fragments of $[Hg(SCN)_{3-n}Cl_n]^-$ connected by shortened secondary intermolecular Hg...N contacts (2.77(2) for (I) and 2.75(8)A and 2.98(8)A for (II) that is much less than the sum of Hg and N Van der Vaals radii.
As a result of these interactions the anion in (I) forms a polymeric chain with one bridge SCN group, while the anion in (II) has a polymeric chain with two bridge SCN groups



(I)



(II)

Chlorine atoms participate in forming shortened contacts Cl...S (3.55(2)A for (I) and 3.58(3)A for (II) with cationic sheets. $[Hg(SCN)Cl_2]^-$ and $[Hg(SCN)_2Cl]^-$ anions are almost planar. Hg atoms displacement from the Cl-S-S or Cl-S-Cl plane is not more than 0.003 A. Hg-Cl or Hg-S bond lengths lie in the range of bond lengths characteristic for other haloid or thiocyanate mercurates.

Conductivity (σ) of (I) is 3-6 $(ohm\ cm)^{-1}$ at room temperature; it increases about ten times upon temperature decrease, reaches maximum at 35 K and then the salt undergoes a sharp metal-insulator transition. Conductivity of (II) is 3-5 $(ohm\ cm)^{-1}$, it monotonously increases upon temperature reduction up to 50 K and then the salt undergoes an insulating transition (fig.3). The only difference between these two salts is the presence of one for I and two for II bridge groups in the anion. It is interesting that anion of less symmetry in I allows to stabilize a metallic state to lower temperatures. σ dependence on pressure, ESR and optical properties of

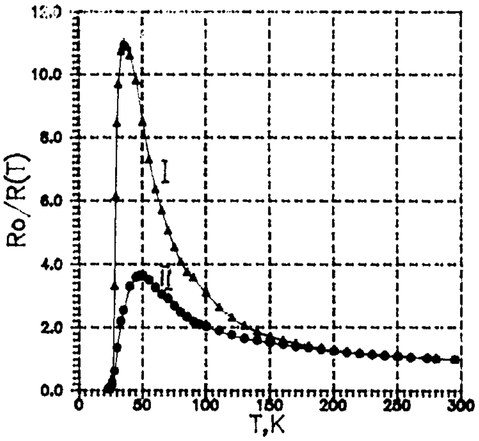


Fig.3.
Temperature dependence of conductivity of I and II.

new organic metals are being under investigation.

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