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Solid state properties and molecular structure of some divalent *n*d^{10} cation-TCNQ salts

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The electrical behaviour of the divalent *n*d^{10} cation-tetracyanoquinodimethane (TCNQ) salts (mercury, zinc and cadmium) has been investigated in the temperature range 300–400 K at a constant pressure of 100 kbar cm^{-2}. The electrical resistivity measurements show a phase transition at nearly 338 and 223 K for $Zn(TCNQ)_2$ and $Hg(TCNQ)_2$, respectively. Collesions between the elucidated structure obtained from the infrared and ultraviolet spectra and the electrical properties of these salts are considered. The activation energy of conductance has been calculated. Further information concerning the electrical behaviour is obtained by considering the type and mechanism of the conduction process. This has been achieved by studying the effect of complex formation and temperature on the mobility of the charge carriers and their production.

1. Introduction

Fully conjugated cyano-compounds such as tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE) are well known to play an important role as strong electron acceptors in the charge-transfer complexes [1, 2]. TCNQ exhibits several exceptional properties of particular interest, such as the ease with which this compound accepts one electron to form simple solid complexes. TCNQ salts with metal cations generally show low to intermediate conductivities (10^{-5}–10^{-2} Ω^{-1} cm^{-1}) at room temperature while its salts with cations of plane aromatic heterocyclic molecules show higher conductivities (10^2 Ω^{-1} cm^{-1}) [3, 4].

Siemons *et al.* [5] reported the electronic properties of some organic and alkali metal TCNQ salts. Their results indicate that for the highest conductivity salts, the electrons degenerate as in metals, while for the less conductive salts the conduction takes place by means of an activated process. Nevertheless, it is not certain whether the carrier production or the carrier motion is activated. Leblance [6] assumed that the conductivity states in the TCNQ salt arise from the motion of the odd electrons along face-to-face stacks of TCNQ molecules and a rearrangement of electrons to give two electrons as neighbours. Further, the energy required for this process is mainly due to Coulomb repulsion between adjacent unpaired electrons.

Fadly and Shabaka [7] studied the electrical behaviour and conduction mechanism of the mixed cation transition metal TCNQ salts in the temperature range 29–533 K. The salts studied were FeCo(TCNQ), FeNi(TCNQ), FeCu(TCNQ), $Fe(TCNQ)_2$ and TCNQ. They attributed the anomaly in the resistivity to the change in the manner of packing between the metal ions and the TCNQ column, together with a change in the periodicity of the TCNQ column at the transition temperature.

The aim of the present work was to study the solid state properties of TCNQ complexes with the divalent nd^{10} cations (Zn^{2+}, Cd^{2+}, Hg^{2+}) where $n = 3, 4, 5$.

2. Experimental procedure

The transition metal TCNQ salts were prepared as previously reported by Melpy *et al.* [8]. The salts studied were $Zn(TCNQ)_2$, $Cd(TCNQ)_2$ and $Hg(TCNQ)_2$. The samples were in the form of discs of 5 mm diameter and 2–3 mm thickness. They were prepared under a pressure of 100 kbar cm^{-2} (10^5 bar $= 1$ Pa). The front faces of the samples were covered with a thin graphite layer to achieve good contact. The cell used in the measurements has been described previously [9]. The temperature was measured by a copper–constantan thermocouple placed close to the sample and the temperature was from 298–398 K. The direct current was measured by a Keithley Electrometer type 610 B.

3. Results and discussion

The electrical resistivity, ρ, of the investigated salts at room temperature (300 ± 2 K) is given in Table I.

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TABLE I Electrical resistivity, ρ, of TCNQ and its transition metal salts at room temperature (300 ± 2 K)

Substance	ρ (Ωcm)
TCNQ	1.1×10^{10}
$Zn(TCNQ)_2$	2.1×10^5
$Cd(TCNQ)_2$	2.5×10^3
$Hg(TCNQ)_2$	5.9×10^{10}

They lie in the range of typical semiconduction resistivity [10]. From Table I it is clear that the resistivity of $Zn(TCNQ)_2$ and $Cd(TCNQ)_2$ are lower by about 10^5–10^7 orders of magnitude than that of neutral TCNQ, while that of $Hg(TCNQ)_2$ is of the same order of magnitude of neutral TCNQ. To correlate the change in the electrical resistivity with the molecular structure changes, the infrared and ultraviolet spectra of these salts are studied. The infrared absorption spectra of these salts is shown in Fig. 1. Although the spectra of the ligand (TCNQ) contains no absorption band at about 1650 cm^{-1}, the different metal compounds absorb with weak to high intensity in this region. This band may be assigned to the aromatic ring vibration, which is a characteristic band for aromatic structure [11], coupled with the C=N stretching vibration. Thus it can be concluded that the quinonoid structure of TCNQ changed into the benzenoid structure.

In the case of mercury complexes the band at 839 cm^{-1} is attributed to the ring stretching vibration of the neutral TCNQ shifted to the lower frequency. The appearance of this band indicates that, in the $Hg(TCNQ)_2$ complexes, both the neutral and the negatively charged TCNQ units are involved in its structure. The electronic absorption spectra of the salts studied are shown in Fig. 2. The band which appears at 260 nm in the ultraviolet spectra of all the salts investigated is almost characteristic of the benzenoid spectra [12]. This supports the idea that the quinonoid structure of neutral TCNQ changed into the benzenoid structure in the complex.

Thus the general decrease in the electrical resistivity of the compounds studied, $Zn(TCNQ)_2$ and $Cd(TCNQ)_2$, above that of the neutral TCNQ, can be interpreted by considering the effect of salt formation upon the electronic and molecular structure of the TCNQ molecule. The infrared and electronic spectroscopic studies showed that the quinonoid structure of the TCNQ molecule changed into a benzenoid structure by complete transformation of an electron to the neutral TCNQ molecule. Thus, the π electronic character of the system will increase with subsequent increase in the π orbital overlap, i.e. the hypothetical orbit radius of the π electrons increases, which increases its delocalization region in the molecule. Therefore, the π electrons become more mobile and the excitation energy will decrease. This will permit a greater participation of the π electrons in the process of conduction and, consequently, the resistivity will decrease. However, the electrical properties of solids are generally determined not only by the properties of its molecule but also by the different possibilities of intermolecular interactions which cannot be totally excluded in this respect.

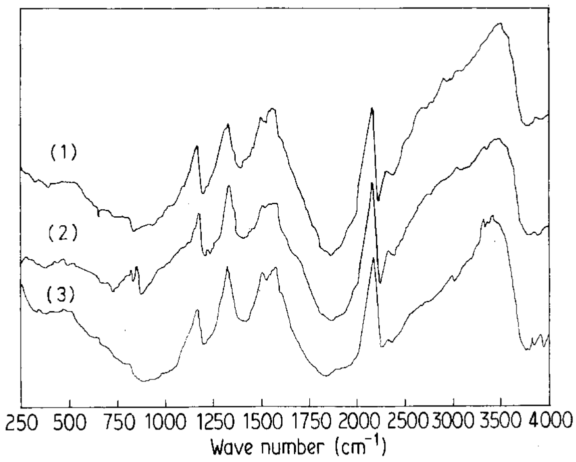

Figure 1 The infrared absorption spectra of the studied divalent transition metal salts: (1) $Cd(TCNQ)_2$, (2) $Hg(TCNQ)_2$ and (3) $Zn(TCNQ)_2$.

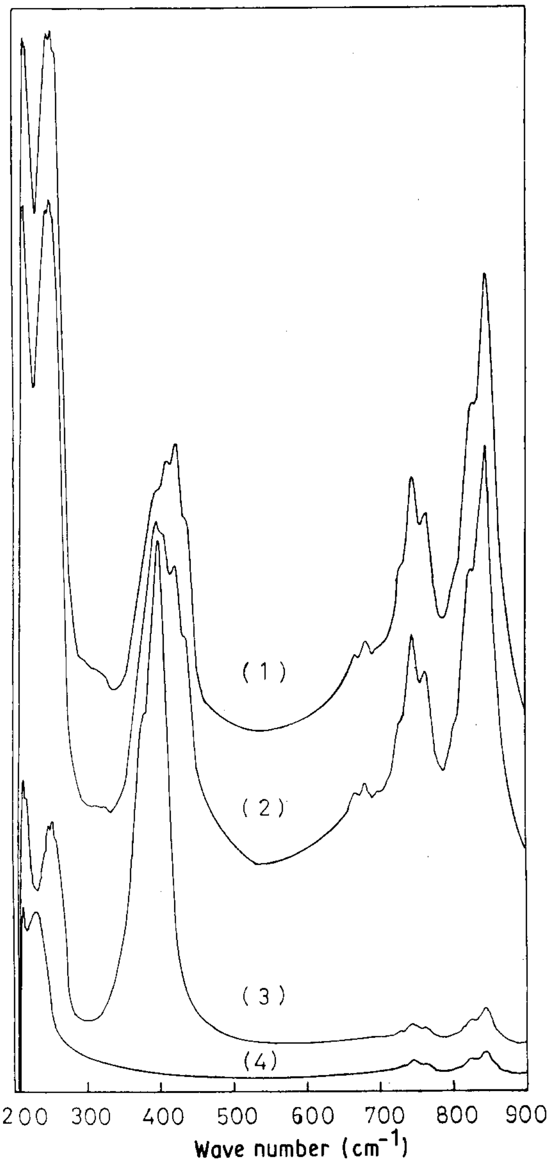

Figure 2 The electronic absorption spectra of the studied divalent transition metal salts: (1) $Zn(TCNQ)_2$, (2) $Cd(TCNQ)_2$, (3) $Hg(TCNQ)_2$ and (4) TCNQ.

X-ray analysis of metal TCNQ complexes [13–17] showed that the TCNQ anions are stacked in a plane-to-plane manner in a column with interplanar distances of 0.32 and 0.35 nm alternate within the row. These values are remarkably smaller than the Van der Waals distance of the interplanar spacing between two aromatic ring planes which is believed usually to be of the order of 0.74 nm [18].

Therefore, the antibonding π^* electron orbitals of the TCNQ amino radicals which are perpendicular to the plane of the ring will overlap with each other. This overlapping will allow a charge transfer between the two anion radicals, with a subsequent decrease in the intermolecular energy barrier, and will facilitate the movement of electron transitions. This is also responsible for the lower electrical resistivity of the TCNQ compounds than the TCNQ itself.

This concept explains the decrease in the electrical resistivity of $Zn(TCNQ)_2$ and $Cd(TCNQ)_2$ compared to the neutral TCNQ.

From Table I, the electrical resistivity of $Hg(TCNQ)_2$ is greater than that of neutral TCNQ. This may be due to the presence of a neutral TCNQ molecule in addition to the TCNQ radical in the complex. This concept is confirmed by the appearance of the characteristic C≡N stretching vibration of the neutral TCNQ in addition to that of the anion radical in the infrared spectra of mercury salts.

The characteristic n–π transition at 260 cm^{-1} which appeared in the ultraviolet spectra confirms the presence of the neutral TCNQ molecule. Also, the increase in the ionic radius of the divalent mercury cation, with 5d orbitals, decreases the overlap integrals of the unpaired electron molecular orbits, which in turn decreases the electrical conductivity, and vice versa [19]. This interpretation is in good agreement with the work done on Cs(TCNQ) complexes which show a higher electrical resistivity than the other alkali metal TCNQ salts [20]. This behaviour is explained on the basis of the presence of a neutral TCNQ molecule in this complex and the greater ionic radius of the 5s orbitals.

The temperature dependence of the electrical resistivity of the salts studied is shown in Fig. 3 and that of TCNQ is plotted for comparison. The linear increase of $\log \rho$ with $1/T$ for the neutral TCNQ and $Cd(TCNQ)_2$ indicates that they behave like typical

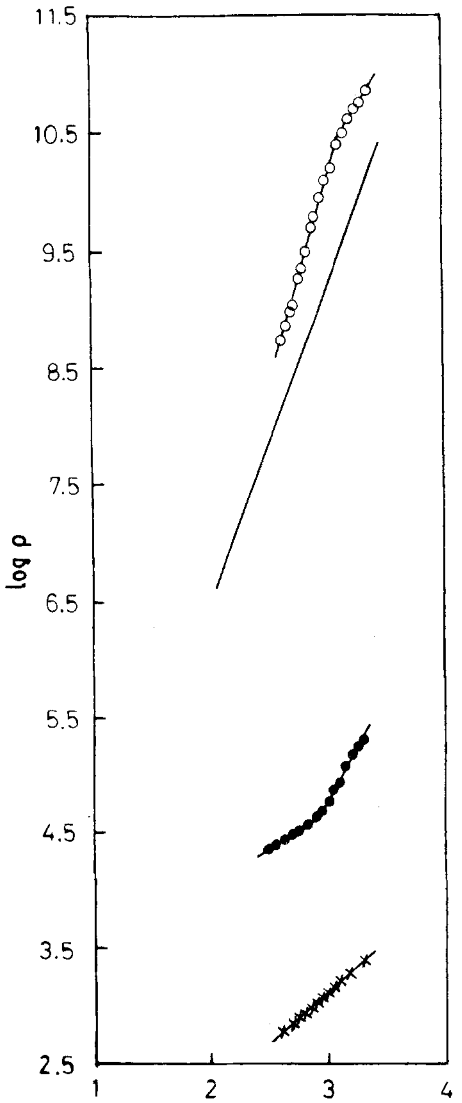

Figure 3 Relation between $\log \rho$ and $1000/T$ for the divalent transition metal TCNQ stalts studied: (—) TCNQ, (●) $Zn(TCNQ)_2$, (×) $Cd(TCNQ)_2$, (○) $Hg(TCNQ)_2$.

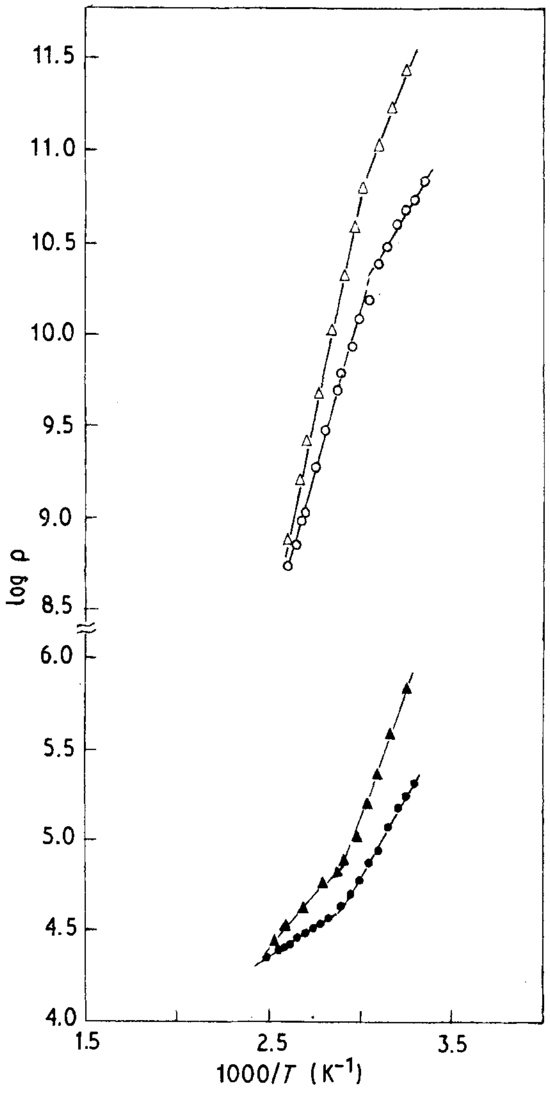

Figure 4 Relation between $\log \rho$ and $1000/T$ on (○, ●) heating and (▲, △) cooling cycles for $Zn(TCNQ)_2$ and $Hg(TCNQ)_2$ salts.

TABLE II Activation energies of the metal TCNQ salts

Substance	E_1 (eV)	E_2 (eV)
TCNQ	0.560	–
$Cd(TCNQ)_2$	0.180	–
$Zn(TCNQ)_2$	0.386	0.127
$Hg(TCNQ)_2$	0.316	0.695

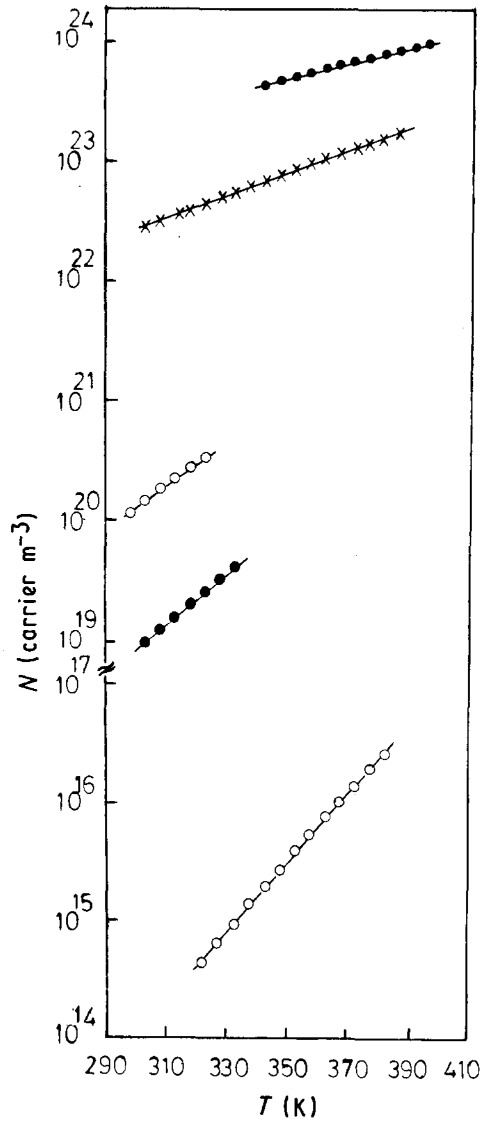

Figure 5 Effect of temperature on the number of carriers for the studied divalent transition metal TCNQ salts: (●) $Zn(TCNQ)_2$, (×) $Cd(TCNQ)_2$, and (○) $Hg(TCNQ)_2$.

intrinsic semiconductor materials. On the other hand, the relation for $Zn(TCNQ)_2$ and $Hg(TCNQ)_2$ salts consists of two linear regions connected with a curved region representing the intermediate temperature region. This anomaly in the electrical resistivity is observed at nearly 338 K for $Zn(TCNQ)_2$ and nearly 323 K for $Hg(TCNQ)_2$.

To gain more insight into the previous anomalies in the electrical behaviour, it is interesting to measure the electrical resistivity on the cooling and heating cycle. Fig. 4 shows that in the thermal cycle of $Zn(TCNQ)_2$ and $Hg(TCNQ)_2$, slightly higher resistivity values are obtained during the cooling cycle than during the initial heating. At room temperature the resistivity in the second thermal cycle is little higher than the initial value. However, the agreement of the transition temperature, T_t, in the heating and cooling processes is obvious. This indicates that the anomaly in the electrical resistivity is not a decomposition process.

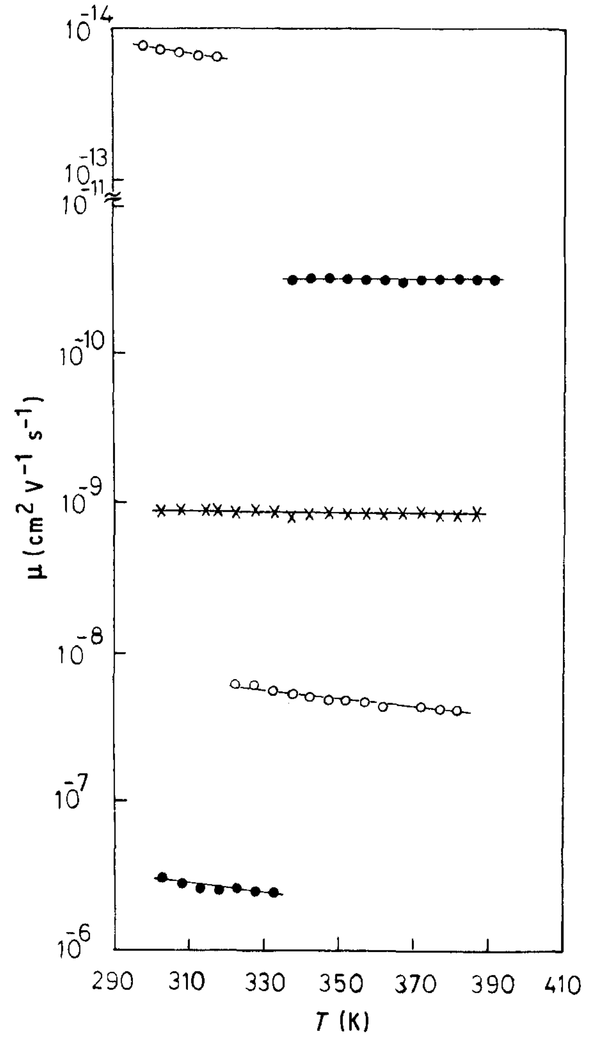

Figure 6 Effect of temperature on the carrier mobility for the studied divalent transition metal TCNQ salts: (●) $Zn(TCNQ)_2$, (×) $Cd(TCNQ)_2$, and (○) $Hg(TCNQ)_2$.

Because TCNQ and its metal salts are composed of units stacked in a plane-to-plane manner, with some periodicity in the column, the anomaly may be principally the result of a change in the manner of packing between the metal ions and the TCNQ column, together with a change in the periodicity of the TCNQ column at the transition temperature.

The activation energies have been calculated from the slope of the linear parts of Fig. 3 and are given in Table II. E_1 and E_2 are the activation energies for $T \simeq T_t$. They are in the range 0.386–0.316 eV for $T < T_t$ and from 0.127–0.695 eV for $T > T_t$.

The change in the activation energy at the transition temperature may be attributed to a change in the type of packing of the stacks in the column and a change in the inter-molecular forces. This change would be expected to cause a change in the singlet–triplet separation energy which depends on the ionic radius and the electrostatic character of the divalent nd^{10} configuration of the cation.

Further information concerning the solid state properties was obtained by considering the type and mechanism of the conduction process. This can be achieved by studying the effect of temperature on the mobility, μ, and the number of current carriers, N, which take part in the conduction process. The number of charge carriers can be obtained by calculating the Fermi distribution function and the density of state function [21, 22]. The product of the two functions gives the actual number of carriers per cubic metre, N. The mobility of the charge carriers μ ($cm^2 V^{-1} s^{-1}$) is also calculated using the single model relation [23]

$$\sigma = Ne\mu \tag{1}$$

where σ is the electrical conductivity ($\Omega^{-1} cm^{-1}$) and e is the electronic charge.

The effect of temperature on the number of carriers and its mobilities for the salts studied is shown in Figs 5 and 6. Inspection of the figures shows that the mobility of the carriers for $Cd(TCNQ)_2$ over the whole temperature range, and for $Zn(TCNQ)_2$ for $T > T_t$ is nearly constant with increasing temperature, while the density of the carriers increases with increasing temperature. This indicates that the activation process in these ranges is due to the electron transfer from the valence band to the conduction band by thermal activation.

The mobility of the carriers for $Hg(TCNQ)_2$ over the whole temperature range and for $Zn(TCNQ)_2$ for $T < T_t$ increases with increasing temperature while the carrier number, N, increases with increasing temperature (Figs 5 and 6). This indicates that the conduction process in these ranges is a contribution from the increased drift velocity of the carriers, as well as their concentration.

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