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# SPECTROSCOPIC INVESTIGATION OF (2,5-DM-DCNQI)$_2$M MATERIALS IN BULK AND THIN FILM FORMS

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## INTRODUCTION

Recently, a new class of electron acceptors based on N,N'-dicyanoquinonediimine (DCNQI), and a number of their charge-transfer complexes and anion radical salts have been prepared (1-5). Among them the compound (2,5-DM-DCNQI)$_2$Cu has attracted special interest,because it exhibits very high electrical conductivity (up to $5\times10^5$ S cm$^{-1}$ below 10 K) and retains its metallic behavior down to 1.3 K without metal-insulator transition (3). Anion radical salts with other counterions exhibit lower conductivities and are semiconductors, or undergo a Peierls transition in the temperature range 100-150 K (4).

To understand such differences in transport properties, various studies have been undertaken, including structural investigations (6-9), pressure effects (10-12), XPS, ESR and susceptibility measurements (5,7,13). These studies have led to the quite general agreement that the properties of the copper salts can be understood on the basis of the mixed-valence state of copper, *i.e.* a formal oxidation state of +1.3 . Thus, it has been suggested that a mixing of copper 3d$_{xy}$ orbital with the pπ LUMO of DCNQI takes place, causing the suppression of the one-dimensional character of the copper-DCNQI compound. Recently, evidence for such an interaction

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was reported by Yakushi et al. (14) on the basis of the optical reflectance spectra of $(2,5\text{-DM-DCNQI})_2M$ (M=Cu, Na) compounds. It was shown that the Cu-compound exhibits an additional absorption at ca. 12,000 $cm^{-1}$, assigned to a charge-transfer between Cu ions and DCNQI anions.

It has been demonstrated, in the case of TCNQ-based materials, that vibrational spectroscopy is a useful tool in studying the state of the acceptor species, the knowledge of which is essential in understanding the materials properties (15). In this paper we wish to report on the Raman, infrared and uv-vis spectra of $(2,5\text{-DM-DCNQI})_2M$ (M=Cu, Ag, Na) materials. Thin film formability of the Cu- and Ag-compounds has been also investigated, and preliminary results are reported here.

## EXPERIMENTAL

2,5-DM-DCNQI was synthesized according to the published procedure (1). The anion radical salts of Cu and Na were prepared upon reduction of the acceptor by the corresponding metal iodide, while silver powder was used as the reducing agent for the preparation of the Ag-salt (4). These reactions were carried out in $CH_3CN$, and resulted in the powders of the anion radical salts. For spectral measurements, free-standing pellets were pressed from the prepared compounds.

Infrared spectra were recorded in the reflectance mode on a Fourier-transform Bruker IFS 113v spectrometer. The appropriate sources, beam splitters and detectors were utilized to cover effectively the 30-5,000 $cm^{-1}$ spectral range. Reflectance spectra in the nir-vis-uv region (4,000-40,000 $cm^{-1}$) were recorded on a Varian 2390 spectrometer. Raman spectra were measured on a Ramanor HG 2S Jobin-Yvon spectrometer. To avoid sample decomposition, care was taken to maintain the incident laser power as low as possible ( <20 mW), and have the sample in the spinning pellet form.

Thin films of $(2,5\text{-DM-DCNQI})_2M$ (M=Cu, Ag) were prepared by the vacuum deposition and thermal treatment technique employed previously for analogous TCNQ-based materials (16,17). Thus, succesive layers of acceptor and metal were vacuum-deposited on the appropriate substrate to achieve a 2:1 DCNQI:metal molar ratio. The so-obtained thin films were heat-treated at *ca* $150^0$ C for a few minutes, to result in light-blue films for M=Ag and goldish films for M=Cu. Various substrates, such as quartz, KBr or $CaF_2$ were used for transmission spectroscopic measurements covering the mid-infrared to uv spectral range.

## Reflectance Spectra

The reflectance spectra of the compounds studied are shown in Figure 1 in an extended spectral range. The infrared region alone is shown as insert in the same Figure. The spectra of Cu- and Na-salts are quite similar to those reported by Yakushi et al. in the 750-25,000 cm$^{-1}$ range (14). In the high-frequency region both Na- and Ag-salts show bands at *ca.* 13,000 and 28,000 cm$^{-1}$, as well as the onset of absorption at *ca.* 38,000 cm$^{-1}$. We note that a dilute solution of (2,5-DM-DCNQI)$_2$Na in CH$_3$CN exhibits bands at 29,400 and 41,500 cm$^{-1}$, arising presumably from localized or intramolecular excitations of the charged DCNQI species, in analogy with TCNQ compounds (18). Thus, the bands of the solid state spectra at *ca.* 28,000 and 38,000 cm$^{-1}$ are assigned to intramolecular excitations of the DCNQI

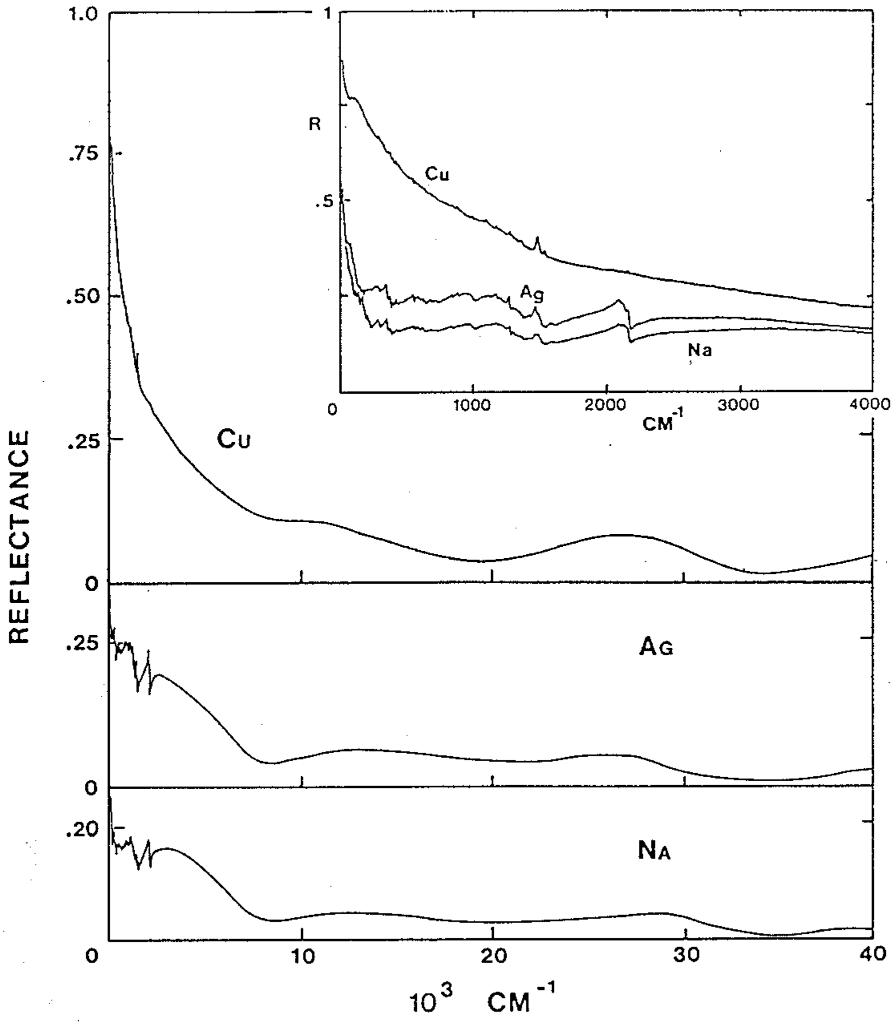

Figure 1. Reflectance spectra of (2,5-DM-DCNQI)$_2$M (M=Cu,Ag,Na) from far-infrared to ultraviolet spectral region. The infrared region alone is shown in the insert.

anion, termed $LE_1$ and $LE_2$ respectively (19). The lower-energy band at *ca.* 13,000 $cm^{-1}$ is assigned to the charge- transfer (CT) excitation between charged DCNQI neighbours along the same stack, denoted $CT_1$ (19). The same feature was assigned by Yakushi et al. to the lowest intramolecular excitation of $DCNQI^{\dot{-}}$ ($LE_1$), on the basis of the similarity of this band with the triplet (15,000 , 16,500 and 17,900 $cm^{-1}$) observed in a solution of 2,5-DM-$DCNQI^{\dot{-}}$. However, we have measured this triplet only in concentrated solutions of $(2,5\text{-DM-DCNQI})_2Na$, indicating that this should be of a charge-transfer, rather than of a localized type (20).

In analogy to the above, the band of the Cu-salt at *ca.* 27,000 $cm^{-1}$ and the onset of absorption at *ca.* 40,000 $cm^{-1}$ are assigned to localized excitations $LE_1$ and $LE_2$, respectively. The broad feature at *ca.* 10,500 $cm^{-1}$ results from contributions of both $CT_1$ type and charge-transfer between copper ion and DCNQI species (14), the latter involving the $3d_{xy}$ orbital of $Cu^+$ and the LUMO orbital of $DCNQI^{\dot{-}}$ (7). A CT transition of the same nature was measured for the first time in CuTCNQ (*ca.* 10,000 $cm^{-1}$) and was attributed to CT from the full d orbitals of $Cu^+$ to LUMO of $TCNQ^{\dot{-}}$ (19).

The infrared conductivity obtained by Kramers-Kronig analysis of the reflectance spectra is shown in Figure 2. The spectra of Na- and Ag-salts show broad but well-defined maxima at *ca.* 4,000 and 3,500 $cm^{-1}$ respectively. These are assigned to CT excitations between a charged and a neutral DCNQI neighbour along the 1-D stacks ($CT_2$) (18, 19). In contrast to this behaviour, the spectrum of the Cu-compound exhibits a very broad absorption, covering effectively the entire infrared region, suggesting the delocalized nature of interactions in this compound, compared to the Na- and Ag-counterparts.

Another pronounced difference in the spectrum of the Cu-salt is observed in the $C\equiv N$ stretching region : both Na- and Ag-salt spectra are characterized by the presence of a strong triplet (*ca.* 2160, 2130 and 2105 $cm^{-1}$), while that of the Cu-salt shows a weak CN absorption in the same region. This effect may well be due to the presence of the broad and strong CT absorption, which effectively masks the $C\equiv N$ absorption of the Cu-compound. In addition, a considerable effect on the $C\equiv N$ stretching could be expected, because of the strong tetrahedral coordination of copper to the nitrogen atoms of the CN groups. This was shown to be manifested by the short Cu-N distance (4,7) and the inter-chain charge-transfer through the $d_{xy}$ orbital of copper (14).

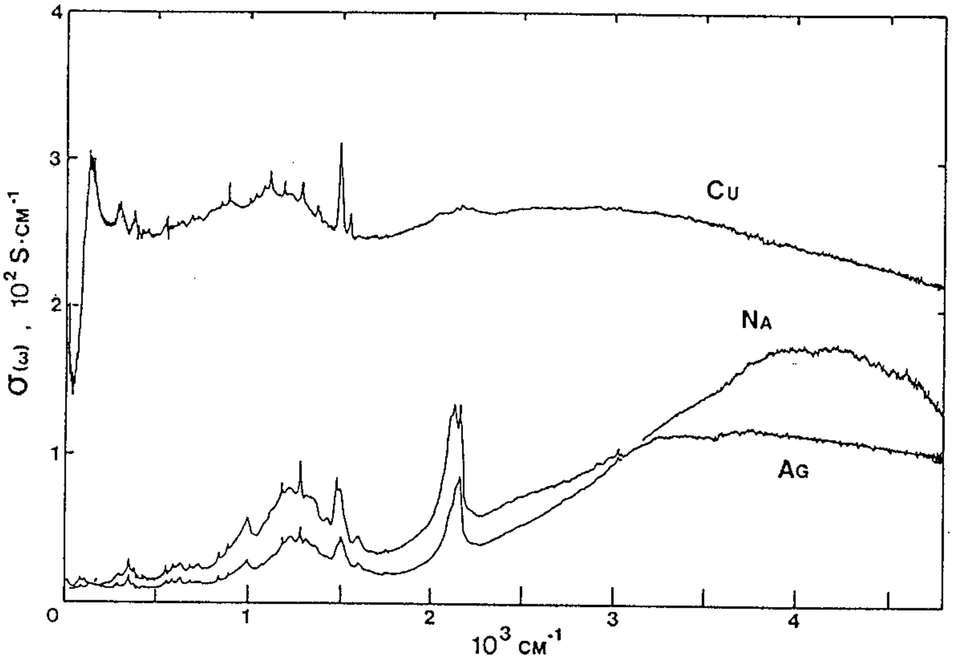

Figure 2. Infrared conductivity of (2,5-DM-DCNQI)$_2$M compounds obtained by Kramers-Kronig analysis of reflectance spectra.

In the lower frequency region (500-2000 cm$^{-1}$) all spectra exhibit similar features, with the noticeable presence of a broad envelope centered at *ca.* 1250 cm$^{-1}$. In the far-infrared, the spectrum of the Cu-salt shows a strong band at *ca.* 140 cm$^{-1}$, which is not present in the rest of the spectra. The origin of this feature can not be identified at present with certainty, but it can be tentatively assigned to the Cu-N vibration, resulting from the strong coordination of Cu.

## Raman Spectra

It was demonstrated for TCNQ compounds that the reduction of the acceptor molecule causes significant vibrational frequency shifts, which are mostly pronounced for the totally symmetric modes (21-23). Thus, the Raman spectra of the three anion radical salts of 2,5-DM-DCNQI have been measured and are presented in Figure 3. The spectrum of the neutral acceptor is also included for comparison. Even though no vibrational analysis for the neutral or charged acceptor has been reported so far, assignments of the main Raman bands can be proposed on the basis of the work on TCNQ compounds (21,22).

The spectrum of the neutral species shows the strongest bands at 2170, 1635 and 1502 cm$^{-1}$. The main activity of the rest of the spectra is also exhibited in the same frequency regions. Clearly, the first band can be assigned to the C≡N

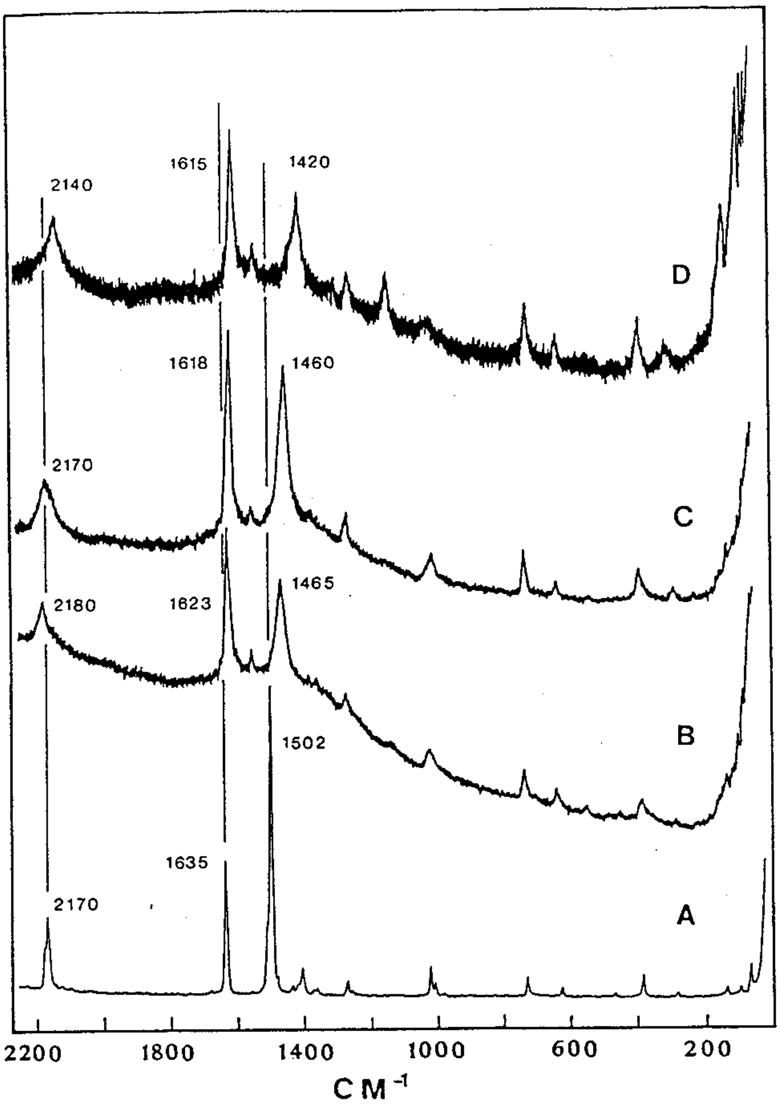

Figure 3. Raman spectra of $(2,5\text{-DM-DCNQI})_2M$ materials in pressed pellet forms (488.0 nm excitation): (A) 2,5-DM-DCNQI; (B) M=Na; (C) M=Ag; (D) M=Cu.

stretching vibration ($\nu_2$), and the second one to the C=C stretching vibration of the ring ($\nu_3$), (the notation used for TCNQ compounds is accepted in this work). The strongest feature at 1502 cm$^{-1}$ is analogous to the $\nu_4$ mode of TCNQ compounds and can be assigned to the C=N stretching vibration (24).

While the spectra of all salts presented in Fig.3 show a considerable broadening in the region of the $\nu_2$ mode, only the spectrum of the Cu-salt exhibits a clear frequency downshift by 30 cm$^{-1}$, compared to that of the neutral acceptor. A similar downshift of the $\nu_2$ mode has been observed in TCNQ compounds (21,22), and found to increase with negative charge on the acceptor molecule (degree of charge-transfer) (23). It should be noted though, that a frequency decrease of the C≡N stretching vibration can also result via a π-back-bonding mechanism, through which electron density is transfered from metal to CN group (25). The opposite mechanism, *i.e.* σ-donation from CN to metal, results in an increase of the CN stretching frequency (25).

The $\nu_3$ and $\nu_4$ modes of the salts appear downshifted, compared to those of the neutral acceptor. The greatest frequency shift is demonstrated by the $\nu_4$ mode of the Cu-salt. It is noted that the frequency of the $\nu_4$ mode of TCNQ compounds was found to change linearly with negative charge on TCNQ-species, *i.e.* the degree of charge-transfer, ρ (23). Assuming that a similar effect holds for DCNQI-compounds, then the Raman spectra of Fig.3 suggest that the negative charge on DCNQI is greater in the Cu-compound, compared to the Na- and Ag-analogs. This result is in agreement with the previous findings, that is the existence of copper ion in a mixed-valence state with a +1.3 average oxidation number.

Spectroscopic studies (ir, uv-vis) of the Cu- and Ag- compounds in thin film forms have also been conducted in the context of this work. The results indicate that the thin film materials are of the same nature with their bulk analogs, and exhibit pronounced orientational effects on various substrates. This work will be reported in detail elsewhere.

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