

Inorganica Chimica Acta

LETTER

Charge transfer in organic electron conductors with coordination complexes determined by infrared absorption spectroscopy

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(Received October 1, 1990)

The physics and chemistry of one-dimensional metals is still an exciting research field [1]. In particular the microscopic description of the formation and population of electron energy bands, responsible for the transport of free charge carriers, is not yet well understood. The electronic conduction in organic molecular crystals of the TTF–TCNQ family (TTF = tetrathiafulvalinium, TCNQ = tetracyano-*p*-quinodimethane) is supposed to arise from a charge transfer (CT) between the constituent donor and acceptor molecules.

It has previously been reported that systems with a degree Z of CT within the limits of $0.4 < Z < 0.7$ usually show metallic behavior [2], while those of Z values below and above that region possess an energy gap between conduction and valence band, leading to semiconductor properties.

The formulation of sufficiently exact relations between Z and, for example, spectroscopic characteristics thus constitutes an important branch of activities in the field of TTF–TCNQ donor–acceptor systems. The availability of reliable experimental data can help to improve existing theoretical models proposed in recent years [3].

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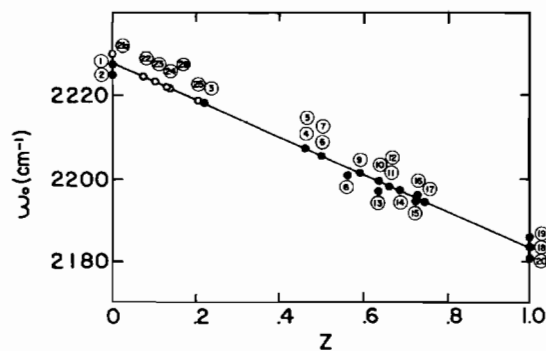


Fig. 1. Nitrile stretching frequency, ω vs. Z for TCNQ complexes. Open circles are frequencies measured by the authors, and added to previously reported data.

TABLE 1. Degree of charge transfer as determined by infrared absorption frequencies of the $C\equiv N$ stretch mode for various TCNQ complexes

Material	Frequency	Z	N
TCNQ	2228	0	1
Cs(2:3)	2225	0	2
TMTSF _R	2219	0.21	3
DBTTF	2208	0.46	4
DPTTF	2208	0.46	5
TEA	2206	0.5	6
MTPP	2206	0.5	7
TMTSF _B	2203	0.57	8
TTF	2202	0.59	9
NMP	2200	0.63	10
EBTTF	2199	0.65	11
TMTTF	2199	0.65	12
TSF	2200	0.63	13
DMTTF	2198	0.68	14
HMDSDTF	2195	0.72	15
HMTTF	2195	0.72	16
HMTSF	2194	0.74	17
Na	2185	1.0	18
K	2183	1.0	19
Cs(2:3)	2181	1.0	20
Pt[HNAFIN] ₂ (a)	2229	0	21a
Pt[HNAFIN] ₂ (b)	2221	0.14	21b
Pd[HNAFIN] ₂	2224	0.09	22
Ni[HNAFIN] ₂	2223	0.11	23
Cu[HNAFIN] ₂	2222	0.13	24
Zn[HNAFIN] ₂	2219	0.20	25

Data for groups 1–20 taken from ref. 4; groups 21–25 reported in this work.

The present paper deals with the determination of the degree of charge transfer, Z , in organic electron conducting systems of the type $M[HNAFIN]_2 \cdot 2TCNQ$ (HNAFIN is *N*-methyl-2-oxy-1-naphthylideneaminato) by infrared absorption spectroscopy, and adds a number of new results to previously published data [4].

The complexes of bis(HNAFIN)Ni(II), Cu(II), Zn(II), Pd(II), Pt(II), were prepared by the method

of Chakravorty and Holm [5], from bis(2-oxy-1-naphthaldehyde)M and methylamine. The methods for the preparation of the 1:2 molecular complexes are practically the same, and, as exemplified by the synthesis of the molecular complexes from Ni[HNAFIN]₂·2TCNQ, a hot acetone diluted solution of TCNQ was added to a hot chloroform diluted solution of Ni[HNAFIN]₂. After being left standing for several hours, black needle-like crystals separated out. They were collected and dried *in vacuo*.

In Fig. 1 the degree of charge transfer, Z , is drawn against the nitrile stretching frequency, ω , for five compound samples of TCNQ (open circles), beside previously reported data by other authors (full circles). The infrared absorption spectra were taken with a Perkin-Elmer spectrophotometer model 598, using KBr pellets of 13 mm in diameter. Usually the absorption spectra show up the two IR-active modes b_{1a} and b_{2a} [3]. The higher-frequency line has been used here as representative of the nitrile stretching vibration energy. As a well established value, the 2228 cm^{-1} absorption line of TCNQ⁰ serves as one reference point (see number 1 in Fig. 1) of the straight line in Fig. 1, while the end point ($Z = 1$) has been determined as the mean value from a simple K salt, showing the absorption line at 2184 cm^{-1} .

This procedure is supported by the fact that the TTF-TCNQ vibration frequency of 2204 cm^{-1} generates almost exactly the value $Z = 0.59$, determined and affirmed by other methods [6]. The numerical values for the CT are thus in a region where semi-

conductor behavior should occur [2]. Table 1 contains the numbers measured in the course of this work, and makes reference to previously reported data.

The M(HNAFIN)₂·2TCNQ complex supports a range of charge transfer values between zero with Pt(HNAFIN)₂·2TCNQ and 0.2 with the Zn(HNAFIN)₂·2TCNQ complex. Platin compounds exhibit two modifications, one of them amorphous and the other one needle-like (both of black color and metallic shine). Different displacements in the nitrile stretch band go along with differences in the charge transfer value. A more detailed discussion of the split in the nitrile stretching frequency in these complexes is given elsewhere [7].

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