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Complex Radical–Ion Salts of TCNQ (Tetracyanoquinodimethan) with Cyanine Dye and Related Cations

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The electrical conductivities of the complex radical–ion salts of TCNQ (tetracyanoquinodimethan) with cyanine dye and related cations generally increase with an increase in the polarizability of the cation. With large cations, however, the increase expected from the high polarizability is offset by the size of the cation. From the change in conductivity of the complex TCNQ salts accompanying the variation in structure of the corresponding cations, a plausible structure for the complex salts can be postulated.

INTRODUCTION

The physical processes important to electrical conduction in the TCNQ (tetracyanoquinodimethan) radical–ion salts[1] are not known because of a lack of interpretable phenomena usually used to characterize conduction processes in solids, e.g., Kepler and coworkers[2] were unable to observe galvanomagnetic phenomena in their investigation, and the thermoelectric power measured by Siemons *et al.*[3] is not meaningful. LeBlanc[4] observed that the conductivity of the complex salts tends to increase with an increase in the polarizability of the cationic component of the salt. He has proposed that this behavior is consistent with the general approach used by Mott[5] and Hubbard[6] to describe conduction in narrow-band systems where the electron correlation energies approach or exceed the energy width of the conducting states.

The purpose of the work described here is to test further the correlation between the electrical conductivity of the complex radical–ion salts of TCNQ and the polarizability of the cationic component of the salt. We have synthesized a number of complex salts using cyanine dyes as the cations. These cations were selected because the polarizability can be varied with a relatively small change in the structure of the cation. The results of this study support LeBlanc's observation and also show that the conducitivity is influenced by a delicate balance between polarizability and steric factors. These results are in contradiction to those reported by Lupinski and co-workers[7] from a less extensive study of similar salts.

EXPERIMENTAL

Syntheses

The experimental data are shown in Table I. The complex TCNQ salts were prepared by a two-step procedure in which the simple TCNQ salt was first prepared by the reaction of the cyanine iodide with the lithium salt of the TCNQ radical anion. The simple TCNQ salt (1:1 ratio of cyanine: TCNQ) was then converted to the complex TCNQ salt (1:2 ratio of cyanine: TCNQ) by reaction with neutral TCNQ.

Simple Salts

To a solution of cyanine or cyanine-type salt (0.001 mole) in a minimum amount of hot (80°C) acetonitrile (purified by distillation from P_2O_5) under a nitrogen atmosphere is added a warm solution of $Li^+TCNQ\cdot^-$ (0.001 mole) and lithium iodide (0.001 mole) in a minimum amount of water. The reaction solution is allowed to cool to room temperature and the simple TCNQ salt which forms is removed by filtration. If no precipitate forms readily, concentration of the reaction solution may be necessary. If the starting material is an iodide salt, lithium iodide may be omitted.

Complex Salts (from Simple TCNQ Salts)

To a solution of simple TCNQ salt (0.001 mole) in a minimum amount of hot (80°C) acetonitrile (purified by distillation from P_2O_5) under a nitrogen atmosphere is added a hot solution of TCNQ (0.001 mole) in a minimum amount of acetonitrile. The reaction solution is allowed to cool, and the complex TCNQ salt is removed by filtration. If no precipitate forms readily, concentration of the reaction solution may be necessary. Recrystallization, if necessary, may be effected by the use of purified acetonitrile with a small amount of added TCNQ.

Electrical Measurements

Only microscopic crystals were obtained, and therefore the electrical measurements were made on samples prepared as pressed powder bars (compacted at a pressure of about 1 kbar) measuring 1 cm×0.3 cm×0.3 cm. Wire leads were attached to each bar at four equally spaced intervals along its length with air-drying silver.

Resistivity measurements were made by the standard four-probe technique to eliminate the effects of contact resistance. The current source was a variable-voltage dc supply. Both the current through the bar and the voltage across the potential probes were measured by

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[1] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, J. Am. Chem. Soc. **84**, 3374 (1962).

[2] R. G. Kepler, P. E. Bierstedt, and R. E. Merifield, Phys. Rev. Letters **5**, 503 (1960).

[3] W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, J. Chem. Phys. **39**, 3523 (1963).

[4] O. H. LeBlanc, Jr., J. Chem. Phys. **42**, 4307 (1965).

[5] N. F. Mott, Phil. Mag. **6**, 287 (1961).

[6] J. Hubbard, Proc. Roy. Soc. (London) **285A**, 542 (1965).

[7] J. H. Lupinski, K. R. Walter, and L. H. Vogt, Jr., Mol. Cryst. **3**, 241 (1967).

TABLE I. Cyanine cation absorption data and corresponding complex TCNQ salt conductivity data.

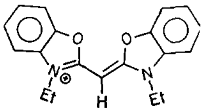
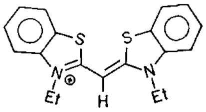
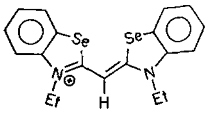
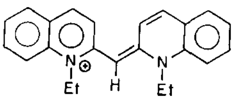
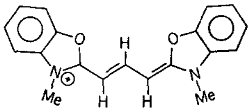
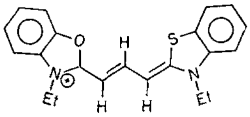
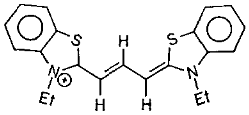
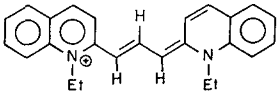
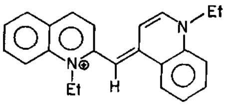
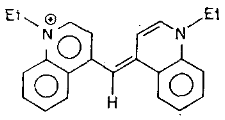
No.	Cation (R^+)	λ_{max} (nm)[a]	σ_{300} (mho/cm)[b]	E_a (eV)[b]	mp (°C)[b]	Anal. (Calc/Found)[b] C	H	N	S
1		375	5.0×10^{-3}	0.27	244–247	72.2 72.5	3.8 3.5	19.6 19.9	
2		423	6.7×10^{-3}	0.21	276–278	69.0 69.4	3.6 3.8	18.7 18.8	8.6 8.3
3		430	4.8×10^{-2}	0.22	288–290	61.4 61.4	3.2 2.9	16.7 16.7	18.8[c] 19.0[c]
4		524	2.8×10^{-1}	0.077	257–258	76.6 76.4	4.2 4.4	19.2 19.3	
5		483	2.6×10^{-1}	0.048	263–266	72.4 72.5	3.5 3.6	19.6 19.5	
6		519	7.0×10^{-1}	0.058	253–255	71.3 71.2	3.9 4.0	18.5 18.5	4.2 4.2
7		557	1.5×10^{-1}	0.067	267–268	69.8 69.8	3.8 4.1	18.1 18.1	8.3 8.3
8		605	2.4×10^{-1}	0.055	250–252	77.2 77.0	4.4 4.5	18.4 18.4	
9		557	4.4×10^{-1}	0.038	249–250	76.7 76.7	4.2 3.9	19.0 19.1	
10		589	1.6×10^{-6}	0.20	217–219	76.7 76.7	4.3 4.8	19.0 18.8	

TABLE I (*Continued*)

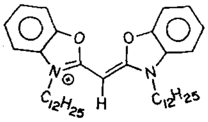
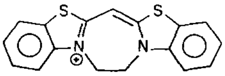
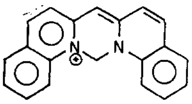
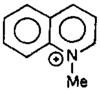
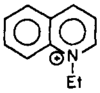
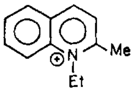
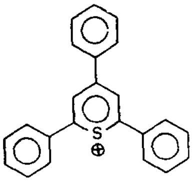
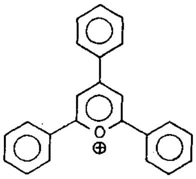
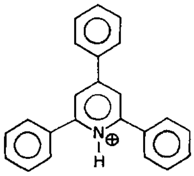
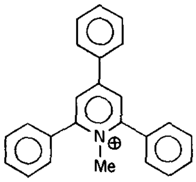
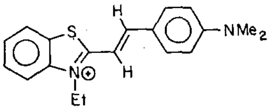
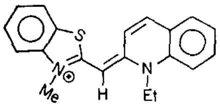
No.	Cation (R^+)	λ_{max} (nm)[a]	σ_{300} (mho/cm)[b]	E_a (eV)[b]	mp (°C)[b]	Anal. (Calc/Found)[b]			
						C	H	N	S
11		377	4.0×10^{-8}		109–110	76.3 76.0	6.4 6.6	14.1 14.4	
12		438	$<10^{-12}$		267–269	68.6 68.7	2.9 3.0	19.6 20.0	8.9 8.6
13		524	8.0×10^{-1}	0.040	273–275	76.4 76.4	3.3 3.4	20.3 19.9	
14			2.4×10^{-1}	0.08	244–245	73.9 74.1	3.3 3.7	22.9 22.9	
15			2.9×10^{-2}	0.15	251–253	74.1 73.8	3.5 3.5	22.4 22.5	
16			1.8×10^{-3}	0.21	209–210	74.5 73.9	3.8 3.7	21.7 21.5	
17		420	8.0×10^{-1}	0.040	256–258	76.9 76.8	3.4 3.8	15.3 15.0	
18		395	3.3×10^{-1}	0.044	288–290	78.7 78.5	3.5 3.6	15.5 15.3	
19		312	3.0×10^{-2}	0.05	183–185	78.8 78.5	3.8 3.7	17.2 17.2	

TABLE I (*Continued*)

No.	Cation (R^+)	λ_{max} (nm)[a]	σ_{300} (mho/cm)[b]	E_a (eV)[b]	Mp (°C)[b]	Anal. (Calc/Found)[b] C	H	N	S
20		308	1.4×10^{-3}	0.15	208–210	79.0 79.2	3.8 3.7	17.3 17.1	
21		525	2.4×10^{-2}	0.066	>350	72.0 72.1	4.0 4.2	19.5 19.8	4.5 4.4
22		483	6.0×10^{-3}	0.28	281–282	72.6 72.4	3.7 3.5	19.3 19.6	4.4 4.7

[a] Longest wavelength absorption for cation only.

[b] Data for complex TCNQ salt—$R^+ (TCNQ)_2^{\cdot -}$.

[c] Selenium analysis.

Kiethley 600-A electrometers. The maximum measurable resistance was 10^9 ohm (conductivities down to about 10^{-8} mho/cm).

The bar was enclosed by a massive brass holder which was suspended in an evacuable quartz tube. This tube was surrounded by a liquid-nitrogen-filled Dewar. Temperatures between 300°K and 80°K were attained by controlling the liquid-nitrogen level and the electrical power dissipated in a resistance heater mounted on the brass sample holder.

The conductivity was unaffected by either prolonged exposure of these solids to pressures of 10^{-4} torr or extended periods of current flow through the samples. The conduction would therefore appear to be electronic. The density of the compact was the same as that measured for the microcrystals by an air pycnometer, and the conductivity was independent of the compacting pressure for pressures above 0.2 kbar.

RESULTS

The room-temperature conductivities and the activation energies obtained for the complex salts of the various cations are shown in Table I. Here the activation energy E is derived from the expression $\sigma = \sigma_0 \exp(-E/kT)$; a relation obeyed quite accurately by all of these salts between room temperature and 80°K.

The pressed-powder technique of sample preparation is an expeditious method, particularly with those salts where only microscopic single crystals can be grown. This technique has, however, obvious limitations when physical interpretations are sought. Repulverizing and repressing several different samples has shown that both σ_{300} and E are reproducible to within 10%. The *N*-methylquinolinium complex salt (**14**) was prepared to compare the results of our procedures with those of Melby *et al.*[1] Our conductivity and activation energy values of 0.24 mho/cm and 0.08 eV compare well with their values of 0.33 and 0.07. Another comparison[1] is the behavior of the 2,4,6-triphenylpyrylium complex salt (**18**). Our values of 0.33 mho/cm and 0.044 eV are equal to or better than their results of 0.06 mho/cm and 0.04 eV.

ESR measurements on the 2,4,6-triphenylpyridinium, -pyrylium, and -thiapyrylium complex salts (**19**), (**18**), and (**17**) show a single, sharp resonance at $g = 2.0038$. Similar behavior is reported by Chestnut[8] in other high-conductivity TCNQ radical–ion salts.

DISCUSSION

The electrical conductivity of complex TCNQ salts will be affected by the crystal structure of the complex salts and the crystal structure will be determined in part by the size and shape of the cation, which we will call hereafter simply a steric effect. It is difficult in general to change significantly the polarizability of the cation without markedly changing its size. From the electrical conductivity alone it is therefore difficult to separate steric and polarizability effects. In the cyanine family, however, one can obtain significant changes in polarizability with only small changes in the morphology of the cation, and thus one can hope that the changes in electrical conductivity are being dominated by the

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[8] D. B. Chestnut and P. Arthur, J. Chem. Phys. 36, 2969 (1962).

changes in the polarizability of these cations. The polarizabilities of the cations we used are not known directly, but can be estimated by calculation from known quantities. The polarizability P (at perturbing field frequencies far below the resonant frequency of the lowest electronic excitation of the cyanine cation) can be expressed in terms of the oscillator strengths f_i and the energies E_i of the optical transitions of the molecules by[9]

$$P = \text{constant} \sum_i (f_i/E_i^2).$$

Because the f_i for all of the π transitions are essentially the same in these molecules, the polarizability scaling is reasonably assigned as being proportional to the wavelength of the longest-wavelength π–π^* transition in these molecules.

The crystal structure of these complexes is unknown. We will assume that, because of their high conductivities, the molecular arrangement is the face-to-face stacking reported[10,11] for the cesium complex TCNQ salt and the N,N,N',N'-tetramethyl-p-phenylenediamine complex TCNQ salt, as is shown in Fig. 1. From the symmetry of the cation, the size of the cation, and the size of TCNQ, possible configurations for the complex salt unit are shown in Figs. 2 and 3. Actually, these configurations may be equivalent, depending on the alignment and displacement (angular and/or lateral) of the stacks.

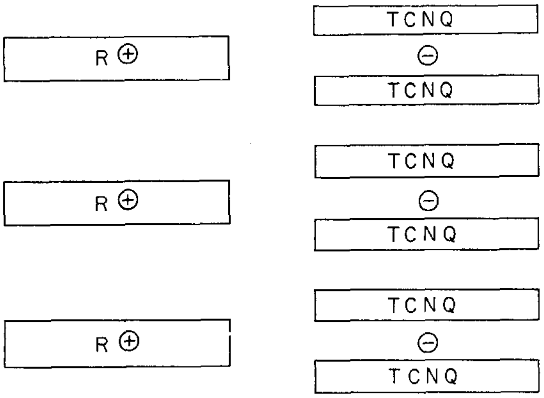

Fig. 1. Side view of a complex TCNQ salt.

For the simple cyanines **1**, **2**, **3**, and **4**, the conductivities of the corresponding complex TCNQ salts generally scale with the polarizabilities, as is best shown by the markedly higher conductivity[12] of the complex TCNQ salt prepared from the simple cyanine **4** with the highest polarizability. For the carbocyanines **5**, **6**, **7**, and **8**, the conductivities of the corresponding complex TCNQ salts are all high. Here we have cyanines with higher polarizability than the simple cyanines, and the corresponding complex TCNQ salts of these carbocyanines are generally more highly conductive. This fact is especially noteworthy because steric effects would tend to work in the opposite direction. Indeed, dicarbocyanines and tricarbocyanines did not form complex TCNQ salts, presumably owing to adverse steric effects which are partly determined by the size of the TCNQ moiety. A delicate balance of steric and polarizability factors is probably operating in the complex salt from carbocyanine **8**.

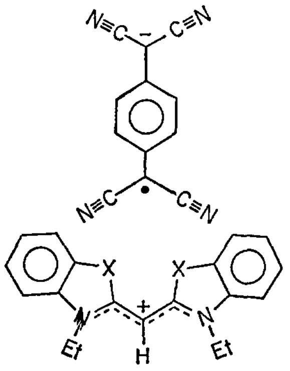

Fig. 2. Top view of a complex TCNQ salt containing a cyanine dye cation.

The interplay of steric and polarizability effects is also evident in the series represented by cyanines **4**, **9**, and **10**. Cyanine **9** is a type of carbocyanine and can be compared with carbocyanines **5–8**, whereas cyanine **10** represents a dicarbocyanine. Polarizability effects dominate in the complex TCNQ salt from **4** and steric effects override in the salt from **10**. A different type of steric effect is represented by cyanines **1** and **11**. The deleterious effect of the dodecyl groups of cyanine **11** upon the conductivity of the corresponding complex TCNQ salt is most likely steric.

The data obtained from the bridged cyanines **12** and **13** lead to the following conclusions. The low conductivity of the complex TCNQ salt from **12** probably accompanies the presence of the ethano bridge which shields the nitrogen centers and may force the TCNQ moieties into a less favorable conformation in the solid state. The complex TCNQ salt of cyanine **13**, however,

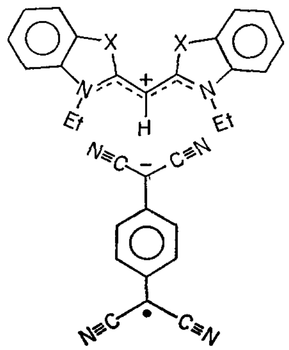

Fig. 3. Alternate top view of a complex TCNQ salt containing a cyanine dye cation.

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[9] W. Kauzmann, *Quantum Chemistry* (Academic Press Inc., New York, 1957), Chap. 16.

[10] P. Arthur, Acta Cryst. **17**, 1176 (1964).

[11] A. W. Hanson, Acta Cryst. **B24**, 768 (1968).

[12] The question of what constitutes a meaningful conductivity difference is not easily answered when working with compacts made from microcrystallites with a large surface-to-volume ratio. We consider changes in conductivity of a factor of 2 to be meaningful.

gives the highest conductivity in the series. This cation is not only rigid and planar, but it does not contain the ethyl groups of the corresponding unbridged cation **4**.

The conductivities of the complex salts of many other cations also display a sensitivity to the type and position of alkyl substituents. A few examples of this presumably steric effect in noncyanine cations are exemplified by the cations **14**, **15**, **16**, **19**, and **20**.

The series exemplified by **17**, **18**, and **19** shows very well the correlation between cation polarizability, $\lambda_{\max}$ of the cation, and the conductivity of the complex TCNQ salt.

The modified cyanines **21** and **22** show the polarizability effect upon the conductivities of the corresponding complex TCNQ salts. The more polarizable cyanine **21** gave the more highly conducting complex TCNQ salt.

A comparison of our results with those of Lupinski *et al.*,[7] demonstrates that, whereas we find a definite correlation of polarizability with conductivity before steric effects take over, they find little correlation of polarizability and conductivity. Considering **4** and **8**, we find roughly the same conductivities for the corresponding complex TCNQ salts, whereas they find the salt corresponding to **8** to be 100 times less conductive than the salt of **4**. In general, their conductivities are lower than ours and probably represent less pure samples, as is evidenced by some discrepancies in their elemental analyses.

We do indeed agree with Lupinski, *et al.*, that the complex salts of TCNQ with cyanine dye cations are not high-temperature superconductors.[13] In fact, we did not observe any superconductivity at 4.2°K for **6**, **13**, and **17**. We also tend to agree that substituting methyl for ethyl groups in the cyanine cations does not noticeably affect the conductivities of the corresponding TCNQ salts: compare the data for cations **5**, **6**, and **7**. For other systems, however, the change from methyl to ethyl substituents can make significant differences, as can be seen from **14** and **15** and from other related compounds such as *N*-methyl- and *N*-ethylacridinium complex TCNQ salts.[14]

The activation energies decrease as the conductivities increase. The significance of activation energies measured on compressed powders is questionable; they probably arise from the extrinsic factors of intercrystallite contacts. In the few cases where single crystals and compacts can be compared,[3] there is essentially no agreement between the activation energies for high conductivity salts. In the salts with lower conductivities (less than 10^{-4} mho/cm), the activation energy in the single crystal is comparable to that in the compact.

Polycrystallinity

If a pressed powder is regarded as a polycrystalline specimen composed of a randomly oriented array of crystallites where the conductivity within each crystallite is highly anisotropic, then the measured conductivity will be an average of the conductivities available in one crystallite. It can then be shown that the measured conductivity σ^* is

$$\sigma^* = 3\sigma_{11}\sigma_{22}\sigma_{33}/(\sigma_{11}\sigma_{22}+\sigma_{11}\sigma_{33}+\sigma_{22}\sigma_{33}),$$

where σ_{11}, σ_{22}, and σ_{33} are the components of the conductivity tensor referred to its principal axis.

If $\sigma_{11} \gg \sigma_{22} \approx \sigma_{33}$, as for *N*-methylquinolinium complex salt,

$$\sigma^* = \tfrac{3}{2}\sigma_{22}$$

and σ^* is heavily weighted in favor of the low-conductivity directions of the crystal. As an example, for the 4-cyano-4-methylquinolinium complex salt,[3] $\sigma_{11}=1$ and $\sigma_{22}=\sigma_{33}=2\times10^{-2}$ mho/cm and $\sigma^*=3\times10^{-2}$ mho/cm. The compact of this salt gives $\sigma^*=2\times10^{-2}$ mho/cm[22] and the agreement with the calculated σ^* is quite good.

The conductivities of compacts of the salts in Table I are comparable to those observed[1,3] for compacts of salts with $\sigma_{11} \approx 10^2$ mho/cm, and therefore it seems reasonable to expect that our materials would show similar properties in single-crystal form.

CONCLUSION

The complex TCNQ radical-ion salts with cyanine cations can be synthesized. The electrical conductivities of these salts tend to increase with the increasing polarizability of the cation. The magnitude of the conductivity appears to be determined by a delicate balance between steric and polarizability effects. Simple tests do not indicate that these salts are superconductors, at least at temperatures between 300°K and 4.2°K.

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[13] See also E. B. Yagubskii, M. L. Khidekel, I. F. Shchegolev, L. I. Buravov, R. B. Lyubovskii, V. B. Stryukov, Zh. Obshch. Khim. **38**, 992 (1968).

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