

STUDIES OF SOME ANION RADICALS
OF TETRACYANOETHYLENE BY
INFRARED SPECTROSCOPY

By

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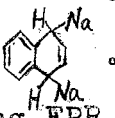
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CHAPTER I

INTRODUCTION

Anion Radicals

It has long been known that certain aromatic hydrocarbons would react with alkali metals to give highly colored adducts. These adducts were thought to be compounds with sigma bonds between carbon atoms and the metals. Such compounds as sodium naphthalenide were represented as . In 1953 it was found that this compound had a strong EPR signal and that the g value for the electron was very close to that of a free electron indicating the compound was actually an anion radical, $\text{Na}^+, [\text{C}_{10}\text{H}_8]^-$ (1).

It has also been found that aromatic or unsaturated hydrocarbons with strongly electron withdrawing substituents such as $-\text{C}=\text{O}$, $-\text{NO}_2$, or $-\text{C}\equiv\text{N}$ would easily form anion radicals. Tetracyanoethylene (ethenetetracarbonitrile or TCNE) with four electron withdrawing groups substituted onto an ethene molecule falls into this category. It is a planar molecule belonging to the symmetry group D_{2h} . The infrared and Raman spectra of TCNE are available and fundamentals have been assigned from 100 to 4000cm^{-1} (2). As expected, TCNE has a high electron affinity (3) and can easily be reduced to the anion radical.

The anion radical of TCNE was first reported by W.D. Phillips, J.C. Rowell, and S.I. Weissman (4). It was found that TCNE reacted in the vapor phase with potassium to give a deep purple solid. An EPR study of solutions of these adducts showed them to be paramagnetic ($g=2.0026$) indicating that the complex formed was $K^+, TCNE^{\ominus}$. Two later papers confirmed this finding and reported in detail the preparation, properties, and reactions of $TCNE^{\ominus}$ (5,6). It was found that TCNE anion radicals could be prepared with metals such as magnesium, aluminum, zinc, sodium, and even copper. These compounds were identified by their infrared spectra which had absorption maxima at 1360, 2180, and 2210cm^{-1} .

The reported infrared spectra of $TCNE^{\ominus}$ are strikingly different (3) from those of the parent compound TCNE. Several fundamentals of TCNE are absent in the anion spectra and an intense new band at 1370 to 1390cm^{-1} appears in the spectra of the anion. Apparently however, $TCNE^{\ominus}$ is quite similar to TCNE in molecular structure. EPR studies of electron exchange between $TCNE^{\ominus}$ and TCNE (4) and fluorescence studies of $TCNE^{\ominus}$ (7) show that $TCNE^{\ominus}$ is formed without severe structural modification except perhaps for small changes in bond length. A study to investigate the unusual infrared spectra of the anion radicals was undertaken by Jack Stanley (8). Samples of $Na^+, TCNE^{\ominus}$ and $K^+, TCNE^{\ominus}$ were prepared under vacuum and studies made of their infrared spectra. These spectra were similar to those reported in the literature. However, it was found that the position of the absorption

bands were slightly different in the spectra of Na^+ , TCNE^- and K^+ , TCNE^- . This indicated that the nature of the cation must play a role in the complex and that there is a back transfer of charge from TCNE^- to the cations. This allowed charge transfer theory to be applied to the anion radical and the Ferguson-Matsen theorem (8) to be used in explaining the spectra of TCNE^- .

CHAPTER II

THEORY

Mulliken's Charge Transfer Theory

Charge transfer complexes have been a subject of intensive study in chemistry. Usually these complexes, such as iodine in benzene, are highly colored and emphasis was placed upon the electronic spectra of the complexes and the nature of the forces holding the complexes together. A quantum mechanical treatment is given by Mulliken (9, 10) for electron donors, D, and electron acceptors, A, in weak 1:1 complexes. In simplified form this attributes to the normal state of the complex a wave function, ψ_N , which may be written as

$\psi_N = a\psi_0(D,A) + b\psi_1(D^+,A^-)$. The symbols ψ_0 and ψ_1 are respectively the wave function for the unbonded state and for the bonded, or dative state, with $a \approx 1$ and $b \ll a$. Mulliken's theory proved satisfactory for interpreting the electronic spectra of charge transfer complexes. The theory predicts that the energy of intermolecular electron excitation will be given by

$$h\nu = I_D - A_A + C$$

where I_D is the ionization potential of the donor, A_A is the electron affinity of the acceptor, and C is a constant

containing coulombic interactions and other energy terms. Linear relationships are obtained by plotting $h\nu$ against I_D for a series of charge transfer complexes using the same acceptor and assuming C constant (16, for example).

The infrared spectra of charge transfer complexes however, were not so easily understood. Often, as well as the absorption bands of the donor and acceptor appearing in the spectra, sometimes with altered intensities, new bands appeared such as the 992cm^{-1} band of benzene in the iodine-benzene complex. This 992cm^{-1} band corresponded to the Raman frequency of the totally symmetric ring breathing vibration in benzene. However, infrared activity of this fundamental is forbidden by symmetry considerations in free benzene. Therefore it was postulated that upon complexing, the symmetry of the complex allowed activation of the Raman mode. However, E.E. Ferguson and F.A. Matsen correctly explained the activation of this vibrational mode as resulting from an oscillation of the ionization potential of benzene during the symmetric vibration (11, 12, 13).

Ferguson-Matsen Theorem

According to the Ferguson-Matsen theorem, there is a change in the vertical ionization potential of benzene during the symmetric ring breathing vibration. Figure 1 shows that during the vibration the vertical ionization potential of the benzene molecules oscillates thereby causing an oscillation of charge from benzene to the iodine. This charge

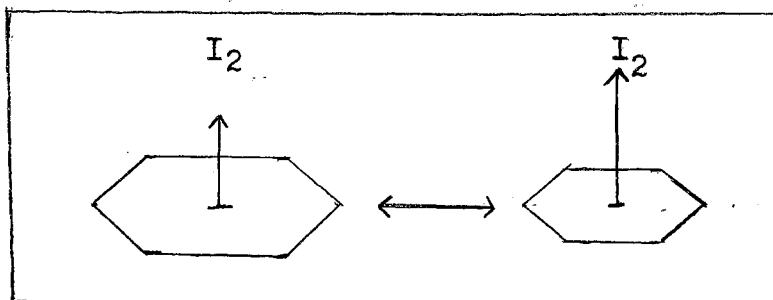


Figure 1. Change in Dipole Moment of the Iodine-Benzene Complex During the Totally Symmetric Ring Stretching Vibration

oscillation causes a change in the dipole moment of the complex perpendicular to the benzene ring as represented by the arrow and hence infrared activation of the totally symmetric ring breathing vibrational mode in benzene. This model has proven quite successful in explaining the infrared spectra of charge transfer complexes.

The Ferguson-Matsen theorem has been successfully applied to charge transfer complexes of TCNE and seems also to apply to the anion radicals of TCNE (8). It has been found (17) that the hexamethylbenzene-TCNE charge transfer complex exists in the solid state as needlelike crystals formed by alternate stacking of the planar hexamethylbenzene and TCNE molecules. As shown for the 1562cm^{-1} band in the complex assigned to the totally symmetric carbon double bond vibration of TCNE in Figure 2 (a), these crystals show dichroism. Infrared studies carried out with polarized radiation showed that spectra made when the crystals were perpendicular to the radiation vector (Figure 2 (a)) were different from those made with the crystals parallel to the radiation vector

(Figure 2 (b)). The enhanced activity of the mode perpendicular to the planes of the molecule was successfully explained by the Ferguson-Matsen theorem although the theorem would predict no activity for the in-plane mode shown in Figure 2 (a). More recent studies by the same research group have shown that the 1562cm^{-1} in-plane activity is absent in spectra of better oriented crystals.

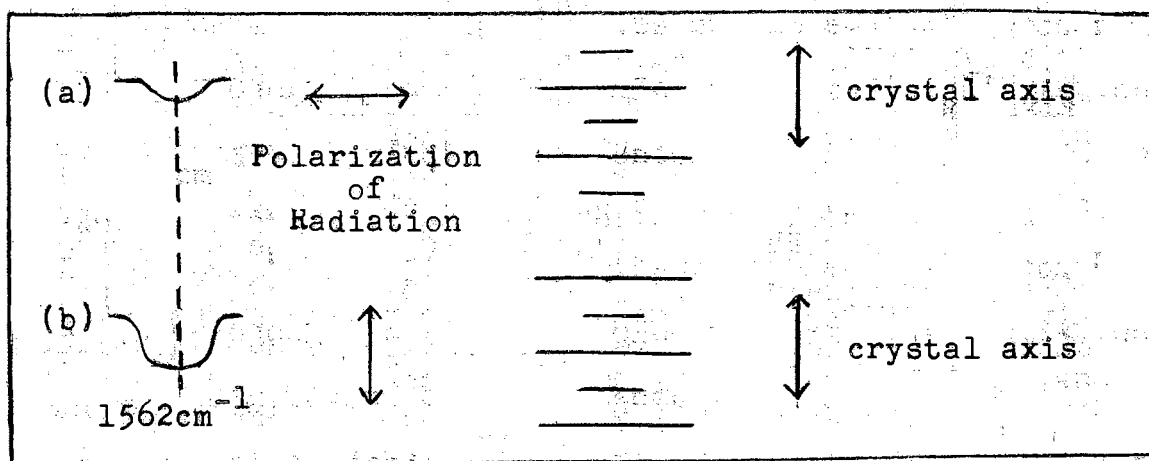


Figure 2. Intensity of the 1562cm^{-1} Band in Hexamethylbenzene-TCNE Complex When Observed with the Radiation Polarized (a) Perpendicular to and (b) Parallel to the Axes of the Crystals

Ferguson and Matsen also established a semi-quantitative relationship between the change in vertical ionization potential of benzene and the change in the polarizability ellipsoid during totally symmetric vibrations (11, 12, 13). Mulliken's description of the wave function for a charge transfer complex is

$$\psi_{N+a}\psi_0(D,A)+b\psi_1(D^+,A^-).$$

For a non polar donor and acceptor, the dipole moment of

the complex would be given by $\mu_N \approx b^2 \mu_1$, where μ_1 is the dipole moment of the dative state. Since μ_1 is invariant, a change in μ_N with a change in a normal coordinate "Q_i" in a complex of benzene would require a change in "b", or

$$\left(\frac{\partial \mu_N}{\partial Q_i}\right)_{Q_i=0} = \left(\frac{\partial b^2 \mu_1}{\partial Q_i}\right)_{Q_i=0} = 2b\mu_1 \left(\frac{\partial b}{\partial Q_i}\right)_{Q_i=0}.$$

Mulliken (10) has shown a relationship between the donor's vertical ionization potential "I" and the dative coefficient "b". Ferguson and Matsen (11, 12) have shown that a relationship exists between "I" and the scalar polarizability, "P", hence $\mu_N \propto b \propto I \propto P$ and

$$\left(\frac{\partial \mu_N}{\partial Q_i}\right)_{Q_i=0} \propto \left(\frac{\partial b}{\partial Q_i}\right)_{Q_i=0} \propto \left(\frac{\partial I}{\partial Q_i}\right)_{Q_i=0} \propto \left(\frac{\partial P}{\partial Q_i}\right)_{Q_i=0}$$

where " \propto " implies a functional relationship. The above relationship implies that a change in the scalar polarizability occurring only in totally symmetric Raman modes gives rise to a change in the dipole moment of the complex and infrared activation of the mode. This results in electron charge being "pumped" from the donor to the acceptor with the frequency of the vibrational mode.

Brown's Vibronic Interaction Theorem

It has been found that the changes in intensities of absorption bands of donors and acceptors upon complexing could be explained in terms of "vibronic interactions" in the π electron system as proposed by Theodore Brown (14, 15). Brown found that during in-plane modes of vibration in phenylacetylenes and in benzene there was a migration of

π electronic charge. This is illustrated in benzene in Figure 3.

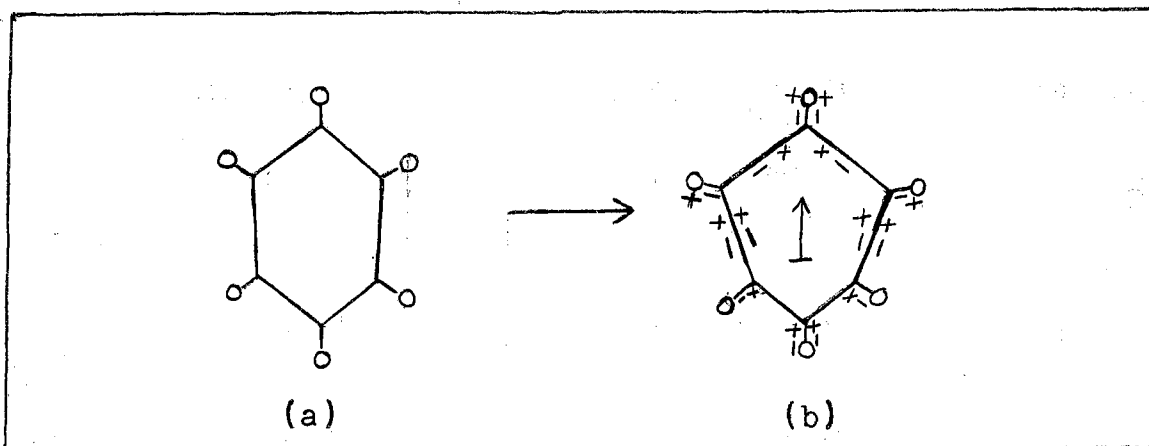


Figure 3. Vibronic Interactions During an In-plane Vibration in Benzene

The small signs in (b) indicate polarization of the σ bond system during the vibration relative to that in the equilibrium configuration (a). The large arrow indicates a dipole representing a migration of π electronic charge during the vibration which in part cancels the dipole formed during the vibration and decreases the intensity of that mode. In complexes where benzene functions as electron donor, part of the π electronic charge would be drawn off, reducing the vibronic interactions and thereby changing the intensities of modes of vibration occurring in the plane of the molecule.

A study of the intensities of spectral bands in TCNE-hexamethylbenzene has been made (18). Upon complexing, a marked increase in the intensity of the 1380cm^{-1} band in

hexamethylbenzene was found and successfully explained by vibronic interaction theory. Upon forming the complex, some of the π electronic cloud was transferred from hexamethylbenzene to TCNE causing a reduction in the vibronic interaction in the hexamethylbenzene and increasing the intensity of the vibrational mode. The increase in π electron charge on the TCNE molecule could have the opposite effect, i.e., the vibronic interaction should decrease the intensities of the in-plane vibrations. A decrease in intensity was found in a study of the 1150cm^{-1} b_{2u} C-C stretch in TCNE upon complexing with hexamethylbenzene.

Application of Theory to Complexes of TCNE

The Ferguson-Matsen theorem and Brown's vibronic interaction theorem have been applied to explain the unusual spectrum of the anion radical of TCNE (8). Figure 4 shows the spectrum of TCNE (a) and of $K^+, TCNE^{\cdot-}$ (b). The main features of the spectra of $K^+, TCNE^{\cdot-}$ are the intense new band at 1370cm^{-1} , the intense new bands at 2200cm^{-1} (The two bands at 2180 and 2201cm^{-1} are believed to result from a single mode split by crystal effects and will be referred to as the 2200cm^{-1} bands.) and the almost complete disappearance of the bands that occur at 800 , 970 , 1170 , 2220 , and 2260cm^{-1} in TCNE. Using the Ferguson-Matsen theorem the intense new bands in the complex at 2200 and 1370cm^{-1} were assigned with the help of a molecular orbital calculation to symmetric Raman modes in TCNE occurring at 2247 and 1569cm^{-1} .

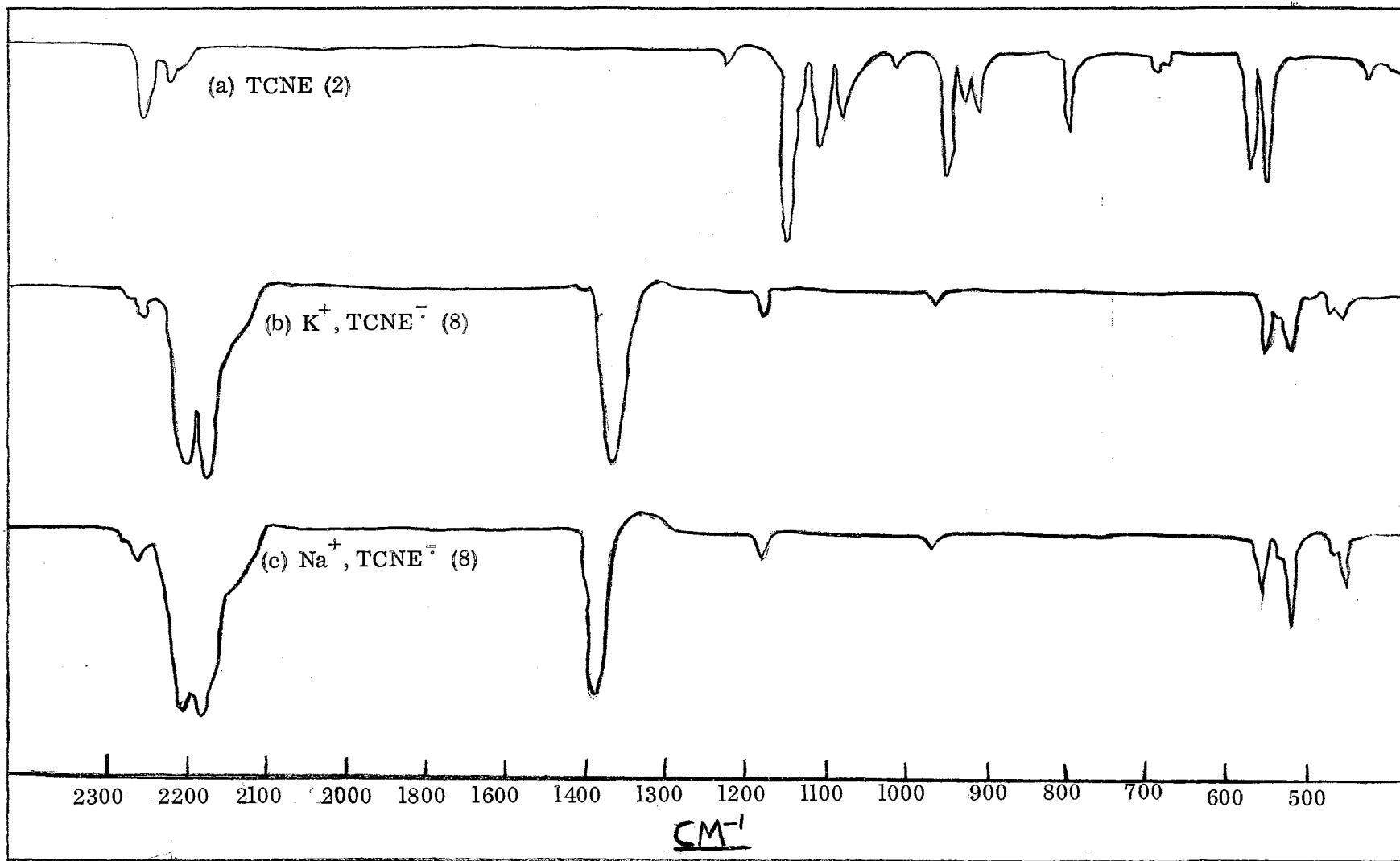


Figure 4. Infrared Spectra of TCNE and TCNE^- Derivatives

The absence of the TCNE infrared fundamentals in the anion spectra was accounted for by vibronic interaction of the electron transferred to TCNE with the dipole moment of the in-plane vibrations. The electron transferred to the π orbital of TCNE is free to move over the plane of the anion and correlates its motion with the dipole formed during planar vibrations. This causes a drastic reduction in the intensity of the normal fundamentals of TCNE.

The electron transferred to TCNE from the alkali metal should enter the lowest energy vacant π orbital of TCNE.

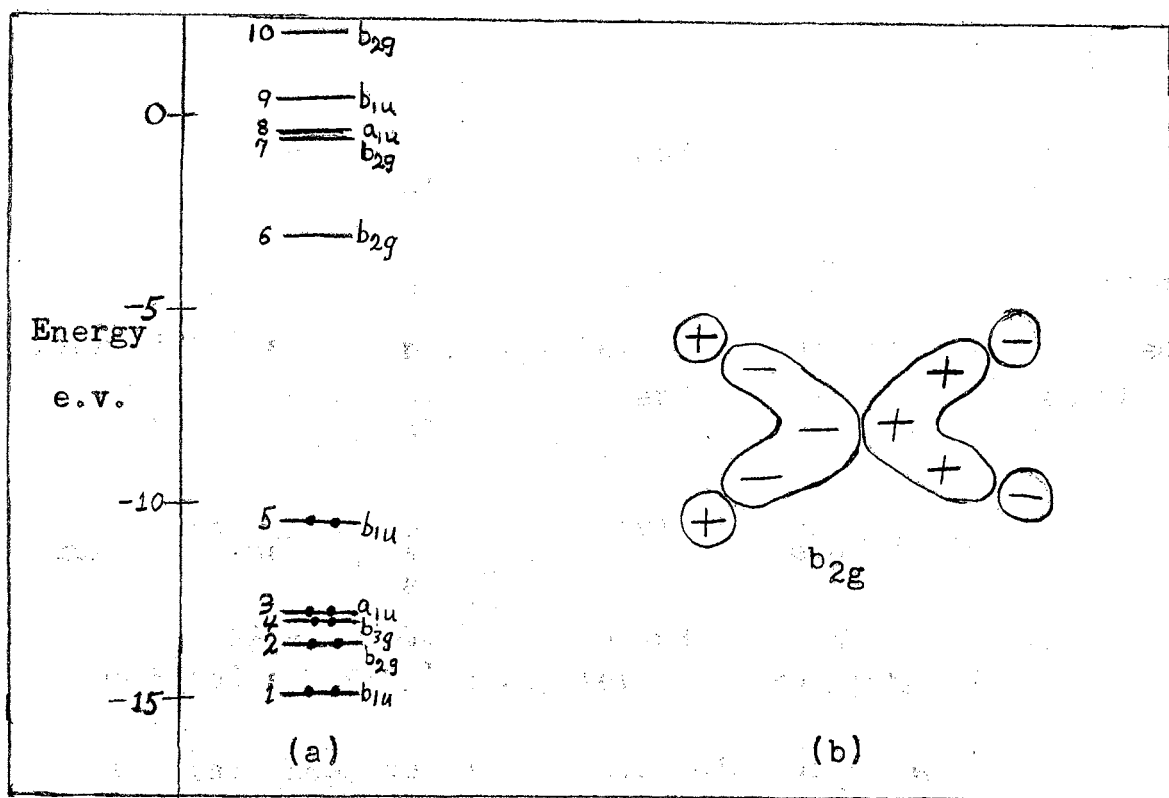


Figure 5. Energy Level Diagram and Shape of Lowest Vacant π Orbital of TCNE

Figure 5 (a) shows an energy level diagram for TCNE obtained

by H. Kuroda, et.al. from a self consistent field molecular orbital calculation (19). The vacant π orbital of lowest energy is the b_{2g} orbital sketched in (b). The orbital is antibonding with respect to the cyanide and olefin bonds and bonding with respect to the carbon single bonds. An electron entering this orbital should reduce the bond order of the $-C\equiv N$ and $C=C$ bonds and cause their stretching frequencies to shift to lower energies while the C-C bonds should increase in bond order and shift to higher energies. The assignments made for the 2200 and 1370cm^{-1} bands in K^+ , $TCNE^{\ominus}$ then agree at least qualitatively with the molecular orbital calculation.

An assignment similar to that made for K^+ , $TCNE^{\ominus}$ can be made for Na^+ , $TCNE^{\ominus}$. However, the absorption bands at 1370 and 2200cm^{-1} in K^+ , $TCNE^{\ominus}$ are found to be shifted toward higher energies in Na^+ , $TCNE^{\ominus}$. This is consistent with the fact that Na^+ has a higher electron affinity than K^+ therefore there should be more backbonding from $TCNE^{\ominus}$ to the cation. This backbonding removes electronic charge from the b_{2g} orbital of $TCNE^{\ominus}$ which increases the bond order of the $C=C$ and $C\equiv N$ bonds and decreases the bond order of the C-C bond. Corresponding shifts are noted in the spectra.

If the proposed model and explanations are correct, they would predict that the positions of the activated Raman bands would be a function of the electron affinity of the cation. This investigation was undertaken to investigate the spectra of anion radicals of TCNE with cations of

varying ionization potentials. Spectra of the anion radicals of Li, Na, K, Cs, Zn, Cd, and Hg would allow the proposed model to be tested and enough information gained perhaps to make further assignments from the infrared spectra of the anion. If the proposed model is correct, it would also allow an estimation of the percent of electron transferred to TCNE by the electron donor in complexes since percent electron transfer would be related to the shift in the vibrational fundamentals upon complexing.

CHAPTER III

EXPERIMENTAL

Apparatus

The anion radicals of tetracyanoethylene are highly reactive toward air and water. Because of this the samples used in this investigation were prepared under vacuum. The essentials of the vacuum system are shown in Figure 6. Liquid nitrogen was used in the trap to condense contaminants, pump oil, and unused reactants. Pressures on the order of 10^{-6} torr could be achieved with the system if sufficient time was allowed for degassing the system.

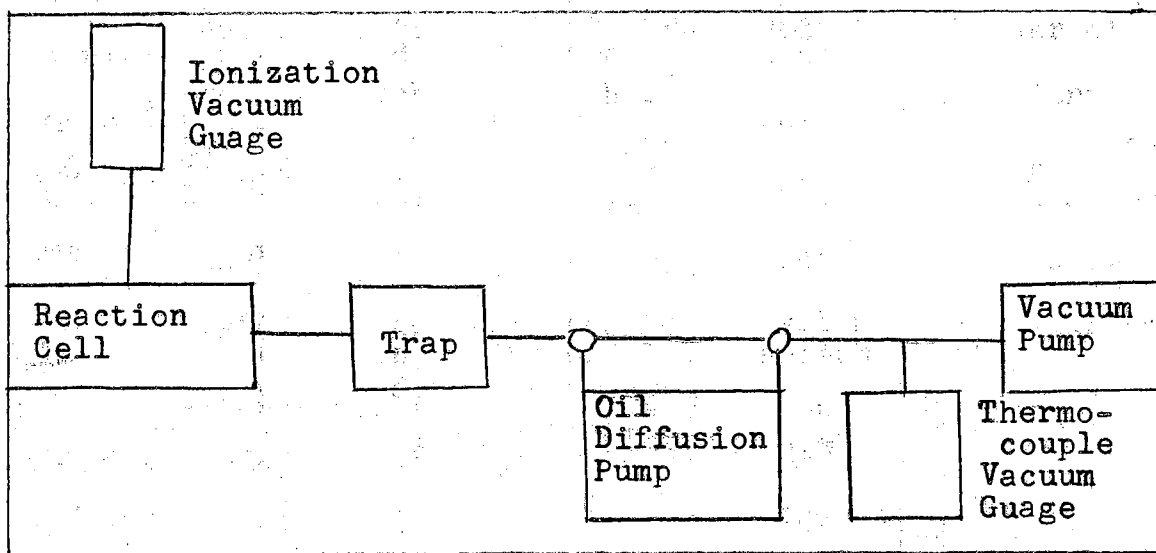


Figure 6. Schematic Diagram of Vacuum Systems Used in Preparing Salts of Tetracyanoethylene

The details of the reaction cell are shown in Figure 7. This cell was devised by Jack Stanley to allow a vacuum preparation of tetracyanoethylene salts by diffusing TCNE and metal onto a CsI crystal attached to a cold finger. The metals were vaporized in a two chamber copper oven (a) heated electrically by ceramic feed throughs, threaded with nichrome resistance wire. These feed throughs were inserted in holes drilled in the copper ovens. The TCNE was vaporized from a glass tube (b) covered with a piece of lead foil with a pin hole in it. The TCNE could be heated with a small ceramic resistance heater (c) to control the rate of sublimation.

The vaporized metal and TCNE reacted in the vapor phase or condensed on the CsI crystal (d) and then reacted. The temperature of the CsI crystal could be lowered by means of a cold finger and dewar (e) to aid in collecting the salts. The cell was constructed with CsI windows (f) so that the dewar and CsI crystal could be rotated 90° after deposition and the sample studied by passing an infrared beam through the windows and the sample.

The ends of the reaction vessel were sealed to copper plates (g) with O-rings. A ceramic feed through (h) allowed electrical connections to be made to the heaters and thermocouples to be placed in the cell to observe the temperature of the ovens. Foil reflectors were added if necessary to reflect heat back to the oven. Connection of the cell to the vacuum system was made through a valve (i) and the pressure of the system measured with an ionization vacuum gauge (h).

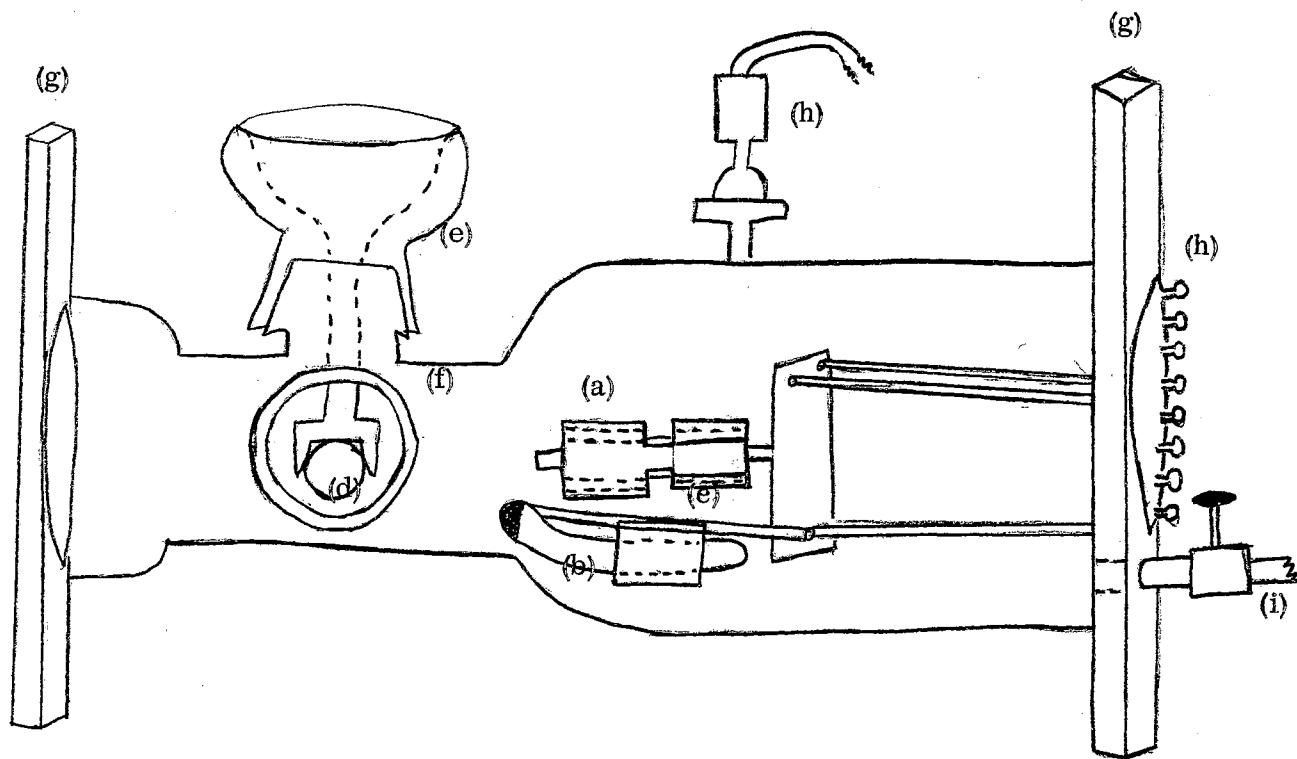


Figure 7. Reaction Cell for Vacuum Preparation and Infrared Sampling of Salts of Tetracyanoethylene

Preparation and Sampling of Salts

Before each reaction the cell was cleaned thoroughly by washing with warm sudsy water to remove unreacted TCNE, metals, and salts which had been deposited. The cell was then rinsed with acetone and dried. The CsI windows were rinsed with absolute alcohol and polished with a tissue wet with absolute alcohol on a glass plate until they were optically clear.

A pyrex tube was loaded with TCNE which had been purified by twice subliming practical grade TCNE. The pyrex tube was capped with lead foil and the tube inserted into the ceramic heater. A small hole was pierced in the lead cap just before the cell was assembled. The oven was then loaded with the metal to be vaporized. The reactive alkali metals were cut into approximately 1/2 gram chunks under kerosene to prevent an oxide crust from forming on the metal. Also, when an alkali metal was used the cell was assembled and evacuated as quickly as possible after the oven was loaded. After the cell was assembled, it was evacuated for about two hours before a reaction was started to remove kerosene left on the metal and other contaminants and to degas the cell.

After a sufficient evacuation period the metal oven was warmed from the front heater to degas the ovens before the

metal melted. Just before the temperature was reached at which the metal vaporized, the TCNE oven was warmed to about 60° to get a stream of TCNE vapor from the pinhole. The CsI window was then rotated into position to receive the sample and the TCNE salt was collected. Since the temperatures of the reactants are the main way of controlling the gases diffusing from the oven, an excess of TCNE was used. The excess TCNE could then be removed by operating the vacuum system for a period of time or by heating the sample by adding warm water to the dewar holding the window. It was found that if the samples were deposited at room temperature, little TCNE was trapped in the sample.

Infrared spectra of the samples were taken immediately upon deposition and then 24 hours later. If the spectra showed excess metal, additional TCNE was vaporized upon the window for a period of time.

Samples of the anion radical of TCNE with sodium, potassium, cesium, and cadmium were prepared by the above method. Attempts to prepare mercury tetracyanoethelenide by this method were unsuccessful. Zinc and lithium were very hard to obtain with the above system. Heat from the hot metal oven warmed the TCNE before the metal was vaporized and the TCNE vapors reacted with the molten metal in the oven. A cold finger was attached to the TCNE oven to keep it at low temperatures until the metal was depositing. A few samples of $\text{Li}^+, \text{TCNE}^-$ were prepared but they were of poor quality. The metal oven often shorted out before the

necessary temperature could be reached. A 10 ohm ceramic heater substituted for the copper oven was found to be satisfactory for vaporizing zinc and lithium.

The infrared spectra of the salts were recorded in the 200 to 4000cm^{-1} region with a Beckmann IR-7 Spectrometer. The spectrum was scanned in the NaCl region from 4000 to 600cm^{-1} by use of NaCl prisms and the better samples were recorded in the CsI region from 200 to 600cm^{-1} by means of a CsI prism interchange. Since the IR-7 is a double beam instrument and the windows of the reaction cell were CsI, a 10cm evacuated gas cell with CsI windows was placed in the reference beam. The background was scanned before each run, but since it was almost flat and remained relatively constant it could be ignored if the cell windows were cleaned and polished before each run.

A sample suitable for Raman spectroscopy was prepared by reaction of potassium iodide with TCNE in acetonitrile under a nitrogen atmosphere. The solution was placed in a glass tube with a flat end, evacuated to remove the solvent and iodine, and sealed by means of a stopcock at one end of the tube. A Raman spectra of the sample could not be obtained, probably because the sample absorbs strongly in the visible region of the spectra. Also, visible spectra were taken of several selected samples. However, infrared spectra taken after the visible spectra showed the samples to have reacted with oxygen and water so the attempt to obtain visible spectra of samples was abandoned.

CHAPTER IV

RESULTS

TCNE anion radicals with Cs, Li, Zn, and Cd have been prepared and infrared spectra obtained of these salts. Although it was originally proposed also to prepare Hg^{+2} , $(\text{TCNE}^{\cdot-})_2$, attempts to prepare it were unsuccessful. TCNE placed in a container with Hg for several weeks showed no evidence of reaction. However, since TCNE vapor could react with Hg whereas TCNE solid might not, several attempts were made to prepare the compound by vaporizing TCNE and Hg together as was done in preparing the other salts. No salt was deposited on the window, but a black appearing deposit was formed on the copper support for the window. This however, appeared to be finely divided Hg and it was not soluble in acetone as $\text{TCNE}^{\cdot-}$ salts are.

The salts of Cs and Li were similar in appearance to the red-purple salts of K and Na. $\text{Cs}^+, \text{TCNE}^{\cdot-}$ appeared to be more red in color while $\text{Li}^+, \text{TCNE}^{\cdot-}$ appeared to be more purple. The salts of the alkali metals deposited at low temperature appeared to be brown, but changed to their characteristic colors as they warmed. The salts of Zn and Cd appeared to be green, with perhaps a slight purplish cast to thick films. It has been suggested that this purple color

might come from an electron transfer between a TCNE anion radical and a neutral TCNE molecule (4), but this is not likely. The color of the alkali metal compounds vary with the cation and weak complexes of TCNE are purple so the color is probably characteristic of the complex.

Spectra for the prepared salts were studied in the spectral region for 200 to 4000cm^{-1} . The spectra are reported only for the region from 400 to 2400cm^{-1} . No infrared activity related to the anion appears in the 2400 to 4000cm^{-1} region and atmospheric absorption and low spectrophotometer energy in the 200 to 400cm^{-1} region makes interpretation very difficult.

Another complication in interpretation is impurities in the spectra. The main ones are unreacted TCNE and the dianion of TCNE. The spectra of TCNE is well known so its bands can be eliminated from the spectra. For the dianion, the cyanide stretching peaks are shifted down about 100cm^{-1} and a broad but weak band occurs from 1260 to 1300cm^{-1} and at 985cm^{-1} . Also, especially on samples kept under vacuum for a length of time, oxidation and hydrolysis reactions occur. The products are reported to be the pentacyanopropenide and tricyanoethenolate of the respective metals (6). The infrared spectra of the pentacyanopropenide ion is reported by C. Looney and J. Downing (20) but that of tricyanoethenolate could not be found. Studies made by deliberately exposing samples to oxygen show that most of the infrared activity of these impurities are in the 1400

to 1600cm^{-1} region of the spectra. Fortunately this is an area in which the anion radical does not absorb. By a careful comparison of the relative intensities of several spectra, the bands of the anion radical can be sorted out from that of the impurities, especially since the impurities are usually present only in very small amounts. In the Figures 8 and 9 used in the discussion, the peaks in the infrared spectra believed to be impurities have been eliminated. However, in Table I, all questionable peaks are recorded along with those of the anions.

Figure 8 shows the spectra of $\text{Cs}^+, \text{TCNE}^-$ and $\text{Li}^+, \text{TCNE}^-$. The main features of interest are the intense bands at 2195, 2178, and 1358cm^{-1} for $\text{Cs}^+, \text{TCNE}^-$; the bands at 2212, 2185, and 1387cm^{-1} for $\text{Li}^+, \text{TCNE}^-$; and the infrared activity in the CsI region (below 700cm^{-1}) of the spectra. These spectra are very similar to the spectra of the sodium and potassium salts of TCNE (Figure 4) except for some slight changes in the position of the major bands, as expected. Slightly anomalous is the 1387cm^{-1} band in $\text{Li}^+, \text{TCNE}^-$ compared to the 1390cm^{-1} band in $\text{Na}^+, \text{TCNE}^-$. This will be discussed further in the following section.

The spectra of the Zn and Cd tetracyanoethylenides are given in Figure 9. The major bands appear at 2218, 2170, 1367, and 1305cm^{-1} in the spectrum of $\text{Cd}^{+2}, (\text{TCNE}^-)_2$. Intense bands appear in the spectrum of $\text{Zn}^{+2}, (\text{TCNE}^-)_2$ at 2210 and 2120cm^{-1} , but the rest of the spectrum is somewhat diffuse. The CsI region of the spectra of the salts

of Zn and Cd appear much the same as those of the alkali metal salts. The only 2:1 complex reported with which these spectra may be compared is barium tetracyanoethylene prepared in solution by S.I. Weissmann (21) who reported peaks in the infrared spectrum at 2220, 2200, 1610, and 1360cm^{-1} . We have assigned the peak at 1610cm^{-1} to oxidation products but otherwise the spectra agree reasonably well considering the different method of preparation and the difference between cations.

Just as it was surprising that the spectra of the alkali metal tetracyanoethylenides appeared so different from the spectra of TCNE, it is equally surprising that the spectra of the Zn and Cd tetracyanoethylenides (Figure 9) are so different from the alkali metal tetracyanoethylenides. (Figure 4 and 8). Some changes could be expected because of a change in crystal structure, but several new bands appear in the spectra of the Zn and Cd salts and the position of the bands do not seem to be consistent with the proposed model. A discussion of this will be given in the following section.

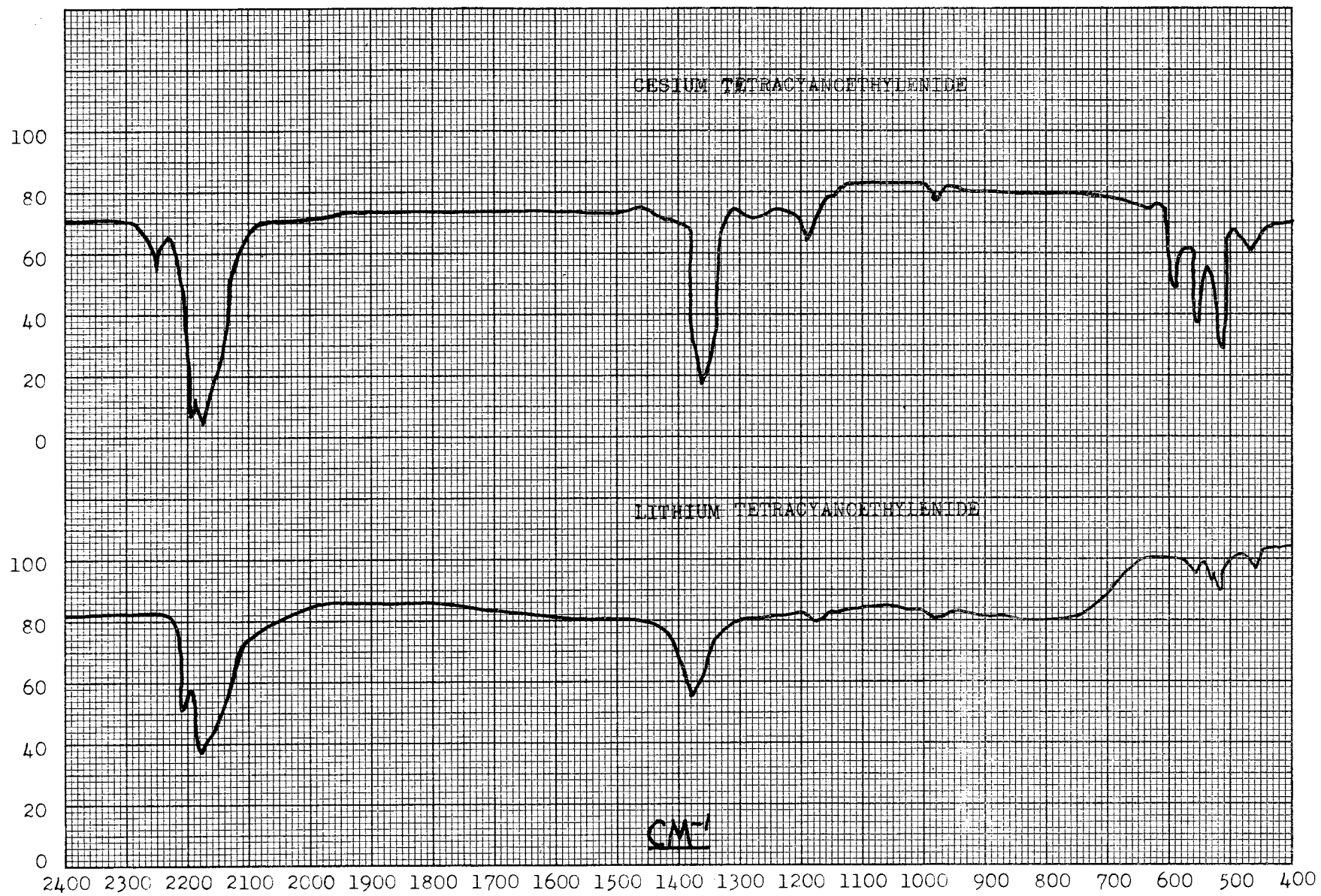


Figure 8. Infrared Spectra of the Anion Radicals of Cesium and Lithium

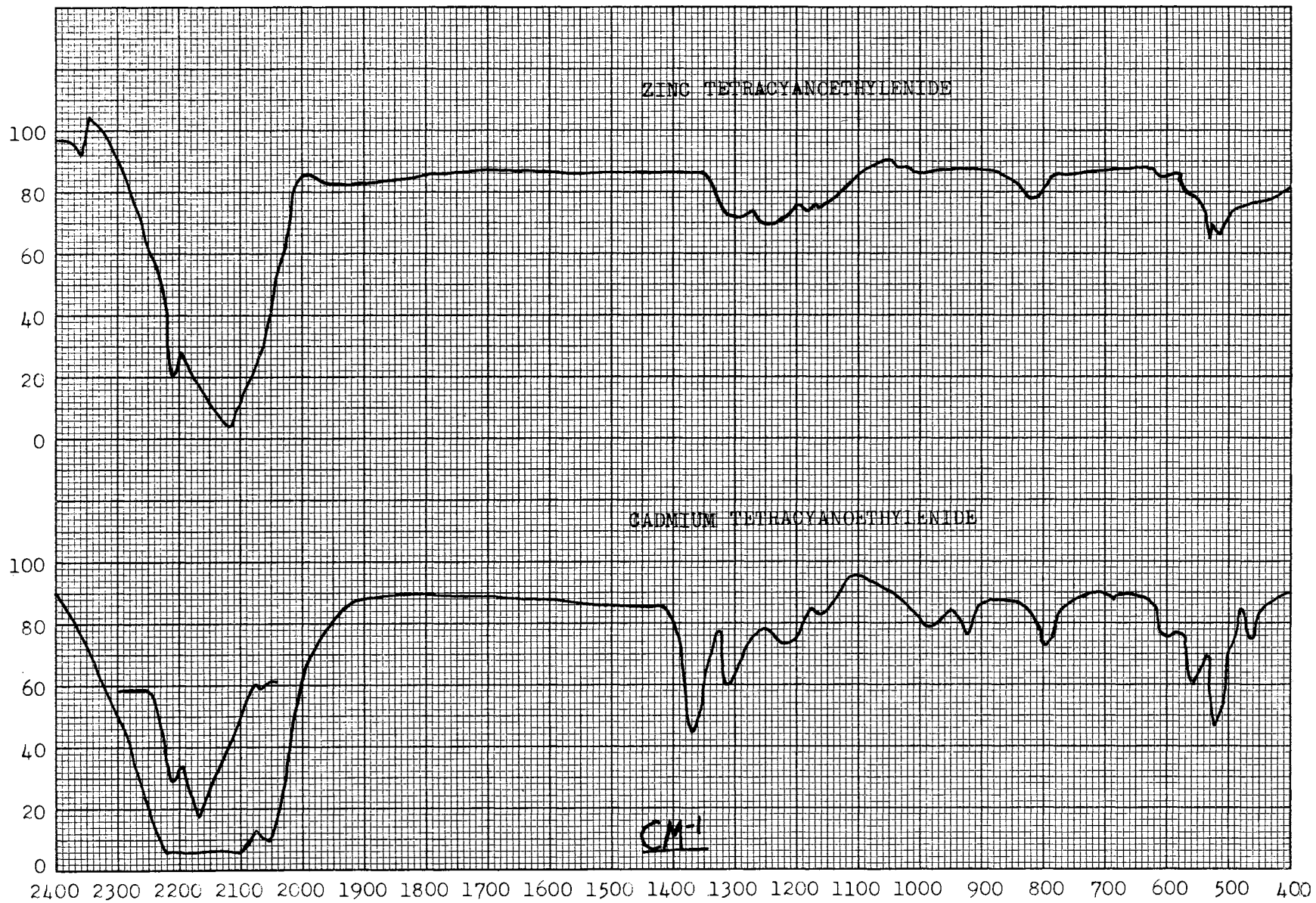


Figure 9. Infrared Spectra of Zinc and Cadmium Tetracyanoethylenides

TABLE I

Frequencies of Major Bands in the Infrared Spectra
in CM^{-1} at 22°C .

<u>Cs^+, TCNE^-</u>		<u>Li^+, TCNE^-</u>	
2260	620	2212 s	554
2195 s*	594	2185 s	527
2178 s	553 s	1575	518
1510	517 s	1387 s	454
1358 s	464	1184	
1290		975	
1190			
975			
<u>Cd^{+2}, $(\text{TCNE}^-)_2$</u>		<u>Zn^{+2}, $(\text{TCNE}^-)_2$</u>	
2218 s	690	2210 s	600
2170 s	600	2120 s	560
1367 s	558 s	1305	530
1305 s	523 s	1245	515
1212	462	1181	
1155		1155	
995		1028	
925		991	
800		810	

*s = strong absorption, all others weak

CHAPTER V

DISCUSSION OF RESULTS

The infrared spectra of the tetracyanoethylenides of cesium and lithium (Figure 8) are very similar to those of the sodium and potassium tetracyanoethylenides (Figure 4) and analogous assignments may be made for the major bands in the spectra. According to the Ferguson-Matsen Theorem, totally symmetric Raman modes of TCNE will be activated in the spectra of the anion radical. These modes are those of a_g symmetry listed in Table II. The absorption bands appearing at 1387cm^{-1} in $\text{Li}^+, \text{TCNE}^-$ and at 1358cm^{-1} in $\text{Cs}^+, \text{TCNE}^-$ can be assigned to the activated C=C stretching mode occurring in the Raman spectra of TCNE at 1569cm^{-1} . These bands are shifted to lower energies because the unpaired electron of the anion radical enters an orbital that is antibonding with respect to the C=C bond (see Figure 5). Since Cs^+ has a lower electron affinity than Li^+ , less backbonding occurs from TCNE^- to Cs^+ and hence the band is red-shifted more for $\text{Cs}^+, \text{TCNE}^-$ than for $\text{Li}^+, \text{TCNE}^-$. The two bands that appear in the spectra at 2212 and 2185cm^{-1} for $\text{Li}^+, \text{TCNE}^-$ and 2195 and 2178cm^{-1} in $\text{Cs}^+, \text{TCNE}^-$ are believed to result from splitting of a single mode by crystal effects. This splitting does not occur

in amorphous deposits of the salts made at liquid nitrogen temperature but the splitting does occur as the sample is allowed to warm and crystallize (8). Assignment then, of these bands to the activated Raman $C\equiv N$ stretch at 2247 cm^{-1} in TCNE would be consistent with the molecular orbital calculation since the electron should enter an orbital on TCNE that is antibonding with respect to the $C\equiv N$ bond. Also, the position of these bands are red-shifted more for the Cs salt than for the Li salt, as expected.

TABLE II
SYMMETRIC RAMAN AND OUT OF PLANE (O.P.)
INFRARED MODES IN TCNE (2)

Symmetry	Species	Activity	Description	CM^{-1}
a_g		R	$C\equiv N$ Stretch	2247^*
			$C=C$ Stretch	1569
			$C-C$ Stretch	679
			$C-C\equiv N$ Bend	541
b_{3u}		IR	$C-C\equiv N$ O.P. Bend	554 ?
			$(CN)-C-(CN)$ O.P. Wag	442 ?

* Reverse assignment from reference (2) as in reference (17)

The cyanide stretching region for the Zn and Cd salts (Figure 9) appear similar to that for the alkali metal salts and similar assignments can be made. However, the proposed model would predict that since Cd^{++} has a higher electron affinity than Li^+ , the position of the $C=C$ stretching mode

would appear at a higher energy than that of Li^+ . The spectra of $\text{Cd}^{+2}, (\text{TCNE}^-)_2$ does not bear this out. The only peak close to the expected value is at 1367cm^{-1} with a slightly less intense peak at 1305cm^{-1} . If the proposed model is correct, it is necessary to explain the position of the C=C stretching band and the origin of the peak at 1305cm^{-1} .

First, it is possible that the 1305cm^{-1} band is not a new mode, but could be assigned to the C=C stretching mode along with the band at 1367cm^{-1} . If in the crystal lattice two anions are strongly associated with one cation, it is possible that their vibrations could couple. This coupling could result in a splitting in energies for the in-phase and out of phase vibrations of the two coupled anions. This splitting also occurs in the C-C stretching vibrations occurring at 1212 and 1155cm^{-1} and at 995 and 925cm^{-1} in the spectrum of cadmium tetracyanoethylenide.

It was at first thought that the backbonding from the TCNE^- to the cation was from the antibonding orbital the electron entered; and, this is probably true in the case of Cs, K, and Na. However, the backbonding need not necessarily be from the orbital the electron entered. In compounds where metals in low oxidation states are bonded to π aromatic systems, the compounds are stabilized by two interactions, (1) a transfer of charge from the metal atom into the lowest antibonding orbital on the π system and (2) a transfer of charge back to orbitals on the metal from a bonding orbital in the π system (22). Hence, there

are two factors causing the C=C stretching mode in TCNE^- to be shifted to lower energies in $\text{Cd}^{+2}, (\text{TCNE}^-)_2$, (1) an electron entering an antibonding orbital and (2) a loss of charge density from a bonding orbital. It is interesting to note that the highest energy bonding orbital in TCNE is the b_{1u} orbital which is bonding with respect to the C=C and C≡N bonds (19). However, since the crystal structure of the complex and the orbitals on Cd participating in backbonding are not known, nothing conclusive can be stated about which TCNE^- orbitals participate in backbonding.

The possibility of TCNE^- backbonding to the cation from a bonding orbital is consistent also with the infrared spectra of the Zn and Li salts. The spectra of the Zn salt, except for the C≡N stretch at 2120 and 2210 cm^{-1} , has very broad and diffuse spectral bands making interpretation difficult. However, a doublet appears at 1305 and 1245 cm^{-1} which can be assigned to the C=C stretching mode. Some backbonding from a bonding orbital probably also takes place in $\text{Li}^+, \text{TCNE}^-$ causing the position of its C=C stretching band to be anomalous to that of the other alkali metal tetracyanoethylenides.

The weak bands in the NaCl region of the spectra and the bands in the CsI region of the spectra also merit some discussion. Weak absorption bands occur in the thicker samples near 2250, 1190, and 980 cm^{-1} . It was thought that these might be TCNE trapped in the sample upon deposition (8). Since the bands near 980 and 1190 cm^{-1} appear as

doublets in the Zn and Cd salts, it appears that these two bands, and also perhaps the band near 2250cm^{-1} , are in-plane modes of TCNE. These modes should be greatly reduced in intensity by vibronic interactions upon formation of the anion since the electron entering the π^* orbital would be free to move over the plane of the molecule and correlate its motion with the dipole formed during the in-plane vibrations.

The major peaks in the CsI region are very much the same for all the salts of TCNE studied. The Ferguson-Matsen Theorem predicts that two symmetric Raman modes of TCNE should be activated in this region on forming the anion radical. These are the symmetric C-C stretch at 679cm^{-1} and the C-C \equiv N bend at 541cm^{-1} (Table II). Although vibronic interactions may greatly reduce the intensity of the in-plane modes of vibration, it should have little effect on the out of plane modes of vibration. These out of plane modes of TCNE are the C-C \equiv N out of plane bend occurring at 554cm^{-1} and the (CN)-C-(CN) out of plane wag at 442cm^{-1} (Table II). Thus, there are four major peaks in the spectra and four modes that should be active. It does not necessarily follow that each band may be assigned to one of these active modes. The C-C symmetric stretch is not very intense in the Raman spectra and it is possible that it is not sufficiently activated to appear in the infrared spectra of the anion radical. It is also possible that combination bands could occur in the spectra in this region, but

this could not be investigated since the spectrum below 400cm^{-1} is not known. However, the spectra in the CsI region are somewhat consistent with the proposed model for the anion radical.

Summary and Conclusions

The purpose of this investigation was to determine the role of the cation in charge transfer complexes of the metal tetracyanoethylenides. $\text{Li}^+, \text{TCNE}^{\ominus}, \text{Cs}^+, \text{TCNE}^{\ominus}, \text{Cd}^{+2}, (\text{TCNE}^{\ominus})_2$ and $\text{Zn}^{+2}, (\text{TCNE}^{\ominus})_2$ were prepared under vacuum by crossing beams of the vaporized reactants and the infrared spectra of the salts were obtained. The Ferguson-Matsen Theorem was used to explain the activation of the symmetric Raman modes in the anion and Brown's vibronic interaction theory adequately explained the wash out of intensity of the in-plane modes of the anion. Predictions made by these theories regarding activity in the CsI region were consistent qualitatively with the spectra. To fit $\text{Cd}^{+2}, (\text{TCNE}^{\ominus})_2$ and $\text{Zn}^{+2}, (\text{TCNE}^{\ominus})_2$ into the model proposed for the alkali metal tetracyanoethylenides, it was necessary to postulate that backbonding from TCNE^{\ominus} to the metal was from a bonding orbital. This successfully explained the unusually large red-shift of the C=C stretching mode in $\text{Cd}^{+2}, (\text{TCNE}^{\ominus})_2$ and $\text{Zn}^{+2}, (\text{TCNE}^{\ominus})_2$ from that in TCNE.

This study indicates that the red-shift in the C=C stretching frequency is not a reliable measure of the percent of electron transfer from donor to TCNE unless it can

be assumed that no backbonding occurs from a bonding orbital on $\text{TCNE}^{\bar{2}}$ to the donor. This assumption would probably be valid for the Cs, K, and Na salts. However, it appears that the electron donated from the alkali metals enters the lowest energy vacant orbital available on TCNE, while in weak complexes the charge is donated to the TCNE orbital of proper symmetry to overlap with the highest energy occupied orbital of the donor (19). Hence a comparison of frequency shifts would give no information about the percent of electron transfer in weak complexes unless the charge from the donor enters only the b_{2g} orbital on TCNE.

Although arguments have been made for the interpretations of the spectra and conclusions given here, these cannot be regarded as definite without further confirmation. A Raman spectra of the anion radical would definitely tell if the assignments made are correct. However, because the anion radicals are highly colored, it may not be possible to obtain a Raman spectra. A study of single crystals or oriented crystals of the anion radical with polarized radiation would provide information about the orientation of the dipole vector formed during symmetric vibrations. X-ray diffraction data would provide information about the position of the cation in the crystal lattice and provide information about the bond distances and, hence, the bond orders in the anion radical. From the bond orders, a force constant calculation could be made which would greatly help in the interpretation of the spectra and allow more definite assignments of the absorption bands in the CsI region.

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