A VIBRATIONAL ANALYSIS OF SODIUM TETRAZOLATE: TETRAZOLE COMPLEXES OF NICKEL(II) AND COPPER(II)

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
LAWRENCE LEE GARBER
1967

This is to certify that the

thesis entitled

A Vibrational Analysis of Sodium Tetrazolate:
Tetrazole Complexes of Nickel (II) and Copper (II).

presented by

Lawrence L Garber

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker, Jr.
Major professor

Date August 2, 1967

O-169

ABSTRACT

A VIBRATIONAL ANALYSIS OF SODIUM TETRAZOLATE: TETRAZOLE COMPLEXES OF NICKEL(II) AND COPPER(II)

by Lawrence Lee Garber

The vibrational analysis of sodium tetrazolate was made by means of a normal coordinate analysis calculation on the tetrazolate ion. The symmetry of the tetrazolate anion is C_{2v}. The calculated A_1 modes are 3124, 1461, 1243, 1138 and 962 cm^{-1}, and may be attributed to the C-H stretch, two symmetric ring deformations, a symmetric ring breathing, and a symmetric ring deformation, respectively. The calculated B_1 modes are 1453, 1063, 1013, and 730 cm^{-1}, and are attributed to the C-H bend and asymmetric ring deformations, respectively. The calculated B_2 modes and A_2 mode are 910 and 456 cm^{-1}, and 537 cm^{-1}, respectively and are attributed to the C-H out-of-plane wag, a ring out-of-plane bend which is asymmetric with respect to the C_2 axis and a ring out-of-plane bend which is symmetric with respect to the C_2 axis, respectively. The observed A_1 vibrational fundamentals, determined from the measurement of the depolarization ratios are 3120, 1290, 1161, and 1065 cm^{-1}. The fifth A_1 mode, 1455 cm^{-1}, was not observed in the Raman spectrum because of masking by the asymmetric 1445 cm^{-1} peak. The observed B_1 modes are 1445, 1023, 1015 and 702 cm^{-1}, while, the observed B_2 modes are 910 and 454 cm^{-1}. The A_2 mode which is Raman active only was not observed experimentally.

Lawrence Lee Garber

The pale-blue complex, bis(tetrazolato)copper(II)monohydrate, is insoluble in all common solvents. The insolubility indicates polymer formation. The complex decomposes when heated and appears from the reflectance spectrum to octahedral and thus six coordinate. Two bands at 328 and 315 cm^{-1} are attributed to Cu-N bonds. The magnetic moment of 1.76 B.M. indicates one unpaired electron.

The complexes bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II), are insoluble in all common solvents (thus suggesting a polymeric structure), decompose when heated and are sensitive to the atmosphere. The reflectance spectra indicate that nickel is in an octahedral environment. The observed d-d transitions are 8.06×10^3 cm^{-1} and 14.7×10^3 cm^{-1}, and 8.33×10^3 cm^{-1} and 14.7×10^3 cm^{-1}, respectively. The transition, $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$, was observed at approximately 25.0×10^3 cm^{-1} for bis(1-methyl-5-tetrazo)nickel(II) and at approximately 26.6×10^3 cm^{-1} for bis(1-cyclohexyl-5-tetrazolyl)nickel(II). Charge transfer bands were observed at 30.9×10^3 cm^{-1} for bis(1-methyl-5-tetrazolyl)nickel(II) and at 35.1×10^3 cm^{-1} and 42.9×10^3 cm^{-1} for bis(1-cyclohexyl-5-tetrazolyl)nickel(II). Bands were observed at 595, 456, and 298 cm^{-1} which may be attributed to the Ni-C bend, Ni-C stretch and the Ni-N bond, respectively, for bis(1-methyl-5-tetrazolyl)nickel(II The Ni-C bend at 581 cm^{-1} and a band at 316 cm^{-1} which may be attributed to a Ni-N bond were observed for bis(1-cyclohexyl-5-tetrazolyl)nickel(II). The observed magnetic moments, 2.90 and 2.98 B.M., for bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II), respectively indicate two unpaired electrons.

A VIBRATIONAL ANALYSIS OF SODIUM TETRAZOLATE: TETRAZOLE COMPLEXES OF NICKEL(II) AND COPPER(II)

By

Lawrence Lee Garber

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1967

547095
12-20-67

Acknowledgment

The author gratefully acknowledges Professor Carl H. Brubaker, Jr. for his guidance, patience and encouragement; and to his wife, Carolyn, whose understanding, assistance and reassurance made this dissertation possible.

The author wishes to express thanks to Dr. L. B. Sims for his aid in supplying the vibrational analysis program and for his assistance in regards to the interpretation of the vibrational analysis data; to Mr. Hans Sachse, who improved the original version of the vibrational analysis program.

Appreciation is extended to Professor Robert C. Taylor and Mr. Harlen Clark, University of Michigan, for the Raman spectra, and to Dr. C. Van Hall, Dow Chemical Company, for the reflectance spectra.

Financial assistance from the National Institutes of Health is gratefully acknowledged.

Table of Contents

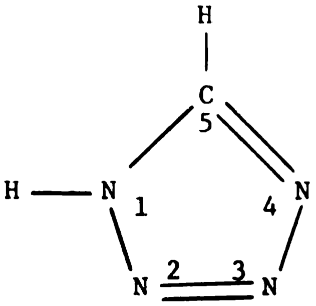
List of Tables

List of Tables (continued)

I. Historical

A. General

Tetrazoles are five membered, heterocyclic ring compounds which contain four nitrogen atoms and one carbon atom. For the structure of the parent compound, tetrazole, with the proper numbering of the atoms refer to I.



I.

Substituents on the tetrazole ring may be present at the 1 and/or the 5 positions. An extensive review of tetrazoles will not be discussed since thorough reviews are presented elsewhere (1,2).

B. Coordination Compounds

Coordination compounds of various tetrazoles have been formed with both nonmetals and various transition metals. Popov, Bisi, and Craft (3) determined, spectrophotometrically, the formation constants of the 1:1 pentamethylenetetrazole (hereafter abbreviated PMT) complexes of iodine monobromide, iodine monochloride, and iodine in carbon tetrachloride solution. Only the PMT-ICl complex could be isolated in a crystalline form. Popov, Wehman, and Vaughn (4) extended this work by investigating, spectrophotometrically, the complexes of iodine monochloride with 7-methyl-,8-sec-butyl-and

8-t-butylPMT. Attempts to isolate these complexes in a crystalline form were unsuccessful. The formation constants indicate that the above complexes are slightly stronger than the corresponding parent PMT-ICl complex. From infrared studies of the I-Cl stretching vibrations by Person, Humphrey, Deskin and Popov (5) it was concluded that PMT is a moderately strong donorand forms complexes with iodine and the interhalogens investigated.

A large number of metal tetrazole coordination compounds have been formed. Bladin (6) prepared the first silver tetrazolate complex and silver complexes of 5-substitutedtetrazolate anions by adding hot silver nitrate to an aqueous solution of the respective tetrazole. Olivera-Mandala and Alagna (7) prepared a canary-yellow tetrachlorobis(1-ethyltetrazole)platinum(IV) complex by adding platinum(IV) chloride to an alcoholic hydrogen chloride mixture of the ligand. Herbst and Garbrecht (8) prepared the silver complexes of 5-substitutedtetrazoles by adding equimolar amounts of silver nitrate to solutions of sodium 5-substitutedtetrazolates. Herbst and Mihina (9) have used silver complexes to aid in the characterization of 5-substitutedtetrazoles. Rheinboldt and Stelliner (10), Dister (11) and Zwikker (12) have reported the preparation of PMT-silver complexes. The stabilities of the complexes in water were not determined. Popov and Holm (13) prepared the silver complexes of PMT, substitutedPMTs and 1-cyclohexyl-5-methyltetrazole in acetonitrile. The complexes were found to be unstable in water and a large excess of ligand was needed to complex even a portion of the silver ion present. The approximate formation constants, determined potentiometrically, were of the order of 10^2. Popov and Holm (13) determined, polarographically, that cobalt(II), thallium(I) and cadmium ion form extremely weak complexes (if any) with PMT, in contrast to the strong tendency of PMT to form complexes with the interhalogens (3,4).

D'Itri and Popov (14,15) have prepared anhydrous complexes of PMT with manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II), copper(I), and zinc(II) perchlorates. The hydrated metal perchlorates were dehydrated with 2,2'-dimethoxypropane. In all cases except copper(I) six moles of PMT were coordinated to the central metal ion. Six coordination was quite unexpected since all previous metal tetrazole complexes have had only two tetrazoles per metal ion (16,17,18,19,20,21) and since PMT is rather bulky. $Cu(PMT)_2ClO_4$ and $Cu(PMT)_4(ClO_4)_2$ were also isolated. X-ray powder patterns indicate that all six coordinated metal complexes are isomorphous. Magnetic susceptibility measurements indicate that the complexes are high spin and hence that PMT is not a strong ligand, a weakness confirmed by the visible absorption spectra. Compared with the free ligand the infrared spectra of the complexes were essentially unchanged.

Kuska, D'Itri and Popov (22) have observed the electron spin resonance spectra for $Mn(PMT)_6(ClO_4)_2$, $Cu(PMT)_6(ClO_4)_2$ and $Cu(PMT)_4(ClO_4)_2$. For the $Mn(PMT)_6(ClO_4)_2$ complex, dispersed in $Zn(PMT)_6(ClO_4)_2$, the data indicate that the metal-ligand bonds are 91 per cent ionic with essentially octahedral symmetry. For the copper complexes it was possible to resolve the copper nuclear hyperfine splittings in the undiluted samples, which is unusual since interactions between neighboring paramagnets are expected to cause significant broadening of the lines so that only $g_{\parallel}$ and $g_{\perp}$ absorptions are resolvable. The symmetry for $Cu(PMT)_6(ClO_4)_2$ is tetragonal with the distortion from octahedral symmetry influenced both by a local Jahn-Teller effect and lattice distortion. As would be expected, $Cu(PMT)_4(ClO_4)_2$ exhibits a definite tetragonal symmetry. The copper-ligand bonds are more covalent than the manganese-ligand bonds, an expected difference.

Brubaker (16) prepared and characterized two crystalline forms of bis(5-aminotetrazolato)copper(II). The visible and ultraviolet spectra suggest coordination rather than simple salt formation. The infrared spectrum indicates that coordination does not involve the amino group. Spectrophotometric studies in aqueous solution gave a formation constant of 10^{12}. Further studies showed similar behavior with tetrazole, 5-phenyltetrazole and 1-ethyltetrazole. A very weak complex is formed between copper(II) ion and 1,5-dimethyltetrazole which, together with relative instability of the silver PMT complex (13), indicates that a replaceable ring hydrogen is necessary for stable complex formation.

Daugherty and Brubaker (17,18) prepared various bis(5-substitutedtetrazolato)copper(II) and nickel(II) complexes by mixing aqueous or alcoholic solutions of the reactants. The nickel(II) forms only impure and poorly characterized complexes in contrast to the copper(II) complexes. In dimethylformamide complexation between nickel(II) and the 5-substitutedtetrazolate anion is clearly indicated from the absorption spectrum. The visible spectrum in solution also indicates that nickel(II) is octahedrally coordinated. The nickel(II) and copper(II) complexes are insoluble in both polar and nonpolar solvents, which suggests polymer formation. When heated, the complexes decompose without melting and cannot be sublimed. When $Cu(NO_3)_2$ was used as a reactant with the 5-aryltetrazoles, no precipitate formed. With $CuSO_4$ or $CuCl_2$ an immediate precipitation ensued. From turbidity studies it was concluded that sulfate or chloride ion is necessary to produce precipitation of the copper complexes.

Jonassen et al., (19,23) have also investigated bis(5-substitutedtetrazolato)iron(II), cobalt(II), nickel(II) and copper(II) dihydrate complexes. The substituent in their studies was strongly electronegative. These complexes also are totally insoluble in polar and nonpolar solvents. The Mössbauer spectra were observed for bis(5-nitro-, 5-chloro- and 5-trifluoromethyltetrazolato)iron(II) complexes. From the absence of observable quadrupole splittings it is concluded that the environment of the metal ion is highly symmetrical, and reflectance spectra indicate that it is octahedral. The magnetic susceptibility for bis(5-trifluoromethyltetrazolato)iron(II) is 1.1 B.M. The reflectance spectrum for this complex indicates that the 5-trifluoromethyltetrazolate anion lies between 2,2'-bipyridine and 1,10-phenanthroline in the spectrochemical series. This, together with the observed low magnetic moment, indicates that the paramagnetic state lies close to the spin-paired ground state. Jonassen, Terry and Harris (20) showed that 5-trifluoromethyltetrazolate anion is a weakly coordinating ligand contrasted with the 5-aminotetrazolate anion (16). Jonassen and Smith (24) have investigated the thermal decomposition of sodium 5-trifluoromethyltetrazolate dihydrate and bis(5-trifluoromethyltetrazolato)iron(II), cobalt(II), nickel(II), and copper(II) dihydrate complexes. These compounds were allowed to pyrolize in a Bendix Time of Flight Mass Spectrometer. The pyrolysis components for each complex are H_2O, CF_3CN, CF_3CN_2, N_2 and $(CN)_2$, and the residues are CoF_3, and NiF_2, FeF_3 and $(NH_4)_2CuF_4(H_2O)_x$. The enthalpy of decomposition was calculated from DTA for the complexes.

Brubaker and Gilbert (21) have prepared various dichlorobis(1-substitutedtetrazole)cobalt(II), nickel(II), platinum(II) and zinc(II) complexes. The nickel, cobalt and platinum complexes are insoluble and all decompose without melting. The zinc complexes are slightly soluble in ethanol and tetrahydrofuran. The stability constants were determined, spectrophotometrically, for nickel(II) complexes with 1-methyltetrazole and 1-cyclohexyltetrazole in absolute ethanol and for cobalt(II) with 1-methyltetrazole and 1-cyclohexyltetrazole in tetrahydrofuran. 1-methyl- and 1-cyclohexyltetrazole complexes of each metal are of comparable strength. For the nickel complexes and the cobalt complexes the overall formation constants are 10^2 and 10^5, respectively. These formation constants are much lower than observed for the bis(5-aminotetrazolato)copper(II) complex (16). The lower formation constants substantiate the idea that a replaceable ring hydrogen is necessary to form stable complexes with substituted tetrazoles. No appreciable difference was observed in the infrared spectra of the complex between the free ligand and the complexed ligand.

Stolle, et al., (25) have reported the preparation of the Grignard reagent of 1-phenyltetrazole(1-phenyl-5-tetrazolylmagnesium iodide). Gilbert (26) attempted to prepare a bis(1-phenyl-5-tetrazolyl)-

nickel(II) complex by reacting the Grignard reagent with anhydrous nickel(II) chloride. The preparation yielded a black solid in all cases. Attempts were made to prove the existance of 1-phenyl-5-tetrazolylmagnesium iodide but were unsuccessful. Attempts to remove the hydrogen ion from the 5-carbon with lithium and sodium amide in liquid ammonia were unsuccessful. The hydrogen bonded to the 5 position is not very acidic.

Beck and Fehlhammer (27), with a novel synthesis, have prepared bis(5-trifluoromethyltetrazolato)bis(triphenylphosphine)palladium(II) by reacting bis(triphenylphosphine)palladium(II) azide with trifluoroacetonitrile in dichloromethane at 0°C. A tetraphenylarsenium tetrakis(1-cyclohexyl-5-tetrazolyl)gold(III) complex was also prepared by the reaction of tetraphenylarsenium tetraazidogold(III) with cyclohexylisonitrile under the same conditions. The proton NMR spectrum (in $DCCl_3$) showed three signals at τ=2.4, 5.2 and 8.3 corresponding to the 20 phenyl protons, the 4 tertiary hydrogen atoms on the cyclohexyl ring and the 40 methylene protons on the cyclohexyl ring, respectively, with the ratios of the intensities, 5:1:10, respectively. The infrared spectrum of the 1-cyclohexyl-5-tetrazolyl ligand is essentially the same as it is for 1-cyclohexyltetrazole.

Holm and Donnelly (28) prepared tetrazolate complexes of iron(II), nickel(II), cadmium(II) and cobalt(II) by the reaction of the corresponding metal salt with tetrazole in water. The iron(II) tetrazolate complex is very poorly defined and is very sensitive to air oxidation. In most cases the complexes are hydrated. From stability constant studies nickel(II) in dimethylformamide forms a very weak complex with

the tetrazolate anion. Infrared studies indicate that the effect of complexation of the tetrazolate anion does not greatly shift the vibrational frequencies.

II. Theoretical

A. Basic Principles of Infrared and Raman Spectroscopy.

Infrared and Raman spectra of molecules are of great importance to chemists for understanding molecular bonding and molecular structural properties. The principles of infrared and Raman spectroscopy have been set forth in detail by a number of authors (29,30,31,32,33,34,35,36,37). Molecules which are absorbing or emitting a quantum of vibrational energy show absorption bands in the region from about 100 to 3500 cm^{-1}. Infrared spectra originate in transitions between two vibrational levels of a molecule in the electronic ground state, whereas, Raman spectra originate in the electronic polarization of a molecule caused by ultraviolet or visible light. If the permanent dipole, $\bar{\mu}$, of a molecule changes as a particular vibration at frequency ν_1 occurs, the molecule will interact with the infrared radiation of ν_1. The intensity of absorption will depend upon $(\partial\mu/\partial Q)^2$ where Q is the displacement from the equilibrium configuration. Thus infrared absorption occurs as a result of a changing dipole moment. In order for Raman absorption to occur, the molecular polarizability, $\bar{\bar{\alpha}}$, must change during the vibration and the intensity will depend upon the $(\partial\alpha/\partial Q)^2$.

Group theory is an invaluable aid in the determination of Raman and/or infrared activity or inactivity of a particular normal vibrational mode of a molecule. Excellent descriptions of the application of group theory to molecular vibrations are presented by Cotton (38), Wilson, *et al.*, (30) and Nakamoto (29).

From Raman spectra it is possible to distinguish between symmetric and asymmetric normal vibrational modes by measuring the depolarization ratio. The basis for the depolarization ratio can be explained by examination of the molecular polarizability tensor, $\bar{\bar{\alpha}}$.

$$\bar{\bar{\alpha}} = \begin{vmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{vmatrix} \tag{2.1}$$

Physically, the various tensor elements of the molecular polarizability will define an ellipsoid. For a totally symmetrical vibration only the diagonal elements of the polarizability tensor change with time, whereas, for an asymmetrical vibration the off diagonal elements change with time and both are associated with the Raman scattering.

If unpolarized light is used to excite a Raman spectrum, the scattering at 90° to the incident light will be found to be at least partially polarized. The extent of polarization depends upon the way in which the polarizability ellipsoid varies during the vibration.

The intensity of an oscillating induced-dipole is

$$I = K\mu_o^2 \tag{2.2}$$

where μ_o is the amplitude of the induced-dipole moment given by

$$\mu = \mu_o \cos 2\pi\nu t \tag{2.3}$$

$$\text{and } K = \frac{16\pi^4\nu^4}{3c^3} \tag{2.4}$$

in which ν is the frequency of oscillation and c is the velocity of light.

The polarizability tensor, $\bar{\bar{\alpha}}$, is related to the induced-dipole moment, $\bar{\mu}$, by

$$\bar{\mu} = \bar{\bar{\alpha}}\,\bar{E} \tag{2.5}$$

where $\bar{E}$ is the electric field vector. Combining equations (2.2) and (2.4) the intensity is

$$I = K\alpha^2E^2 \tag{2.6}$$

If one introduces a nonrotating axes, the total radiation emitted per unit solid angle in the x direction is

$$I = \frac{2\pi^3\nu^4}{c^3}(\mu_{oy}^2 + \mu_{oz}^2) \tag{2.7}$$

For an anisotropic molecule, $\mu_x \neq \mu_y \neq \mu_z$ and are expressed as

$$\begin{aligned} \mu_x &= \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \\ \mu_y &= \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \\ \mu_z &= \alpha_{zx}E_x + \alpha_{zyE_y} + \alpha_{zz}E_z \end{aligned} \tag{2.8}$$

If the direction of propagation of light is coincident with the y axis and if the incident light is plane-polarized with $\bar{E}$ parallel to the direction of observation, i.e., along the x axis, the total intensity observed [$I_T(\text{obs.}\parallel)$] is from equations (2.6), (2.7) and (2.8),

$$I_T(\text{obs.}\parallel) = \frac{2\pi^3\nu^4}{c^3}(\alpha_{yx}^2 + \alpha_{zx}^2)E_o^2 \tag{2.9}$$

where E_o is the amplitude of $\bar{E}$. If the electric field vector is parallel to the z axis (perpendicular to the axis of observation), the intensity, $I_T(\text{obs.}\perp)$, is

$$I_T(\text{obs.}\perp) = \frac{2\pi^3\nu^4}{c^3}(\alpha_{yz}^2 + \alpha_{zz}^2)E_o^2 \qquad (2.10)$$

The intensity, $I_{\parallel}(\text{obs.}\perp)$, of that part of light which is polarized parallel to $\bar{E}$ when $\bar{E}$ is parallel to the z axis is

$$I_{\parallel}(\text{obs.}\perp) = \frac{2\pi^3\nu^4}{c^3}\alpha_{zz}^2E_o^2 \qquad (2.11)$$

From electromagnetic theory the intensity, I_o, of the incident light is related to the amplitude of the electric field by

$$I_o = \frac{c}{8\pi}E_o^2 \qquad (2.12)$$

Upon substitution for E_o^2, equations (2.9), (2.10), (2.11) become

$$I_T(\text{obs.}\parallel) = \frac{16\pi^4\nu^4}{c^4}I_o(\alpha_{yx}^2 + \alpha_{zx}^2) \qquad (2.13)$$

$$I_T(\text{obs.}\perp) = \frac{16\pi^4\nu^4}{c^4}I_o(\alpha_{yz}^2 + \alpha_{zz}^2) \qquad (2.14)$$

$$I_{\parallel}(\text{obs.}\perp) = \frac{16\pi^4\nu^4}{c^4}I_o\alpha_{zz}^2 \qquad (2.15)$$

For N molecules which are freely orientated in space (e.g., a powder or liquid), equations (2.13), (2.14), and (2.15) become

$$I_T(\text{obs.}\parallel) = \frac{16\pi^4\nu^4}{c^4}NI_o\frac{2\beta^2}{15}$$

$$I_T(\mathrm{obs.}\perp) = \frac{16\pi^4\nu^4}{c^4} NI_o\left(\frac{45\gamma^2 + 7\beta^2}{45}\right) \qquad (2.17)$$

$$I_\parallel(\mathrm{obs.}\perp) = \frac{16\pi^4\nu^4}{c^4} NI_o\left(\frac{45\gamma^2 + 4\beta^2}{45}\right) \qquad (2.18)$$

where $\gamma = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

and $\beta^2 = 1/2[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]$

γ is the spherical part of the polarizability and β is the anisotropic part.

The depolarization ratio, ρ, is defined as the ratio of the intensity polarized perpendicular to $\bar{E}$ to the intensity parallel to $\bar{E}$. If plane polarized light is used, the ratios of the intensities are given by

$$\rho_p = \frac{I_T(\mathrm{obs.}\perp) - I_\parallel(\mathrm{obs.}\perp)}{I_\parallel(\mathrm{obs.}\perp)} = \frac{3\beta^2}{45\gamma^2+4\beta^2} \qquad (2.19)$$

For an asymmetric vibration γ equals zero. Therefore ρ_p equals 3/4. For a symmetric vibration γ and β are both non-zero. Therefore ρ_p has the range $0<\rho_p<3/4$.

If unpolarized incident light is used, the intensities observed parallel and perpendicular to the incident light must be considered. The intensity observed parallel to the incident light contributes one-half of its intensity to the parallel and perpendicular components, respectively. The depolarization ratio, ρ_u, becomes

$$\rho_\mu = \frac{I_T(\mathrm{obs.}\perp) - I_\parallel(\mathrm{obs.}\perp) + 1/2\ I_T(\mathrm{obs.}\parallel)}{I_\parallel(\mathrm{obs.}\quad) + 1/2\ I_T(\mathrm{obs.}\parallel)} = \frac{6\beta^2}{45\gamma^2+7\beta^2} \qquad (2.20)$$

Thus for an asymmetric vibration ρ_u equals 6/7 and for a symmetric vibration ρ_u has the range $0<\rho_u<6/7$.

B. Vibrational Analysis (Normal Coordinate Analysis).

The theoretical analysis of a vibrational absorption spectrum is known as vibrational analysis. The method used to perform the vibrational analysis is known as Normal Coordinate Analysis. The principles of Normal Coordinate Analysis are discussed eloquently by a number of authors (29,30,39,40,41,42).

The purpose of performing a normal coordinate analysis is either to calculate force constants from observed eigenvalues (maxima for the vibrational modes) or to predict theoretically the vibrational spectrum from a suitable set of force constants. A normal coordinate analysis also permits one to make vibrational assignments for a particular molecule.

A molecule possesses 3N (N = number of atoms) degrees of freedom of which, for a nonlinear molecule, three are rotational modes and three are translational modes. Thus, there are 3N-6 normal vibrational modes.

The total vibrational energy is a sum of the kinetic energy and the potential energy. To calculate the vibrational frequencies, it is necessary to formulate the potential and kinetic energies in terms of suitable coordinates. Internal coordinates are usually chosen rather than Cartesian displacement coordinates since the force constants in terms of internal coordinates have a clearer physical meaning and a set of internal coordinates does not involve the translational and rotational motion of the molecule.

A relationship between the internal coordinates and Cartesian coordiantes is needed. If R_t represents one of the 3N-6 internal coordinates and x_i one of the 3N displacement coordinates, the relationship will have the form

$$R_t = \sum_{i=1}^{3N} B_{ti} x_i \quad (t = 1,2,\ldots, 3N-6) \tag{2.21}$$

where the coefficients B_{ti} are constants determined by the geometry of the molecule. Equation (2.21) is expressed in matrix form as

$$\underline{R} = \underline{B}\ \underline{X} \tag{2.22}$$

where $\underline{R}$ and $\underline{X}$ are column matrices of the internal and displacement coordinates, respectively.

The potential energy, V, expressed in terms of internal coordinates is

$$2V = \sum_{i=1}^{n} f_{ii}(\Delta R_i)^2 + \sum_{i \neq j=1}^{n'} f_{ij}(\Delta R_i)(\Delta R_j) \tag{2.23}$$

where, $n = n'$ is the number of internal coordinates, f_{ii} is the force constant of the ith internal coordinate, f_{ij} is the interaction force constant, and R_i and R_j are the internal coordinates, or

$$2V = \sum_{i=1}^{3N-6} f_{ij} \Delta R_i \Delta R_j \quad (j = 1,2,\ldots, 3N-6) \tag{2.24}$$

Expressed in matrix form

$$2V = \underline{R}'\ \underline{F}\ \underline{R} \tag{2.25}$$

where $\underline{R}$ is a column matrix, $\underline{R}'$ is its transpose and $\underline{F}$ is the force constant matrix.

Since the kinetic energy, T, of a particle of mass M and velocity V is given by $2T = MV^2$, the total kinetic energy of a molecule is given by

$$2T = \sum_{i=1}^{3N} m_i \dot{x}_i^{\,2} \tag{2.26}$$

where m_i is the mass associated with the displacement coordinate x_i and $\dot{x}_i$ is the time derivative of x_i. The kinetic energy is not easily expressed in terms of internal coordinates. By defining a set of quantities G_{kl} as

$$G_{kl} = \sum_{i=1}^{3N} B_{ki}\ B_{li}/m_i \quad (k,\ l = 1,\ 2, \ldots,\ 3N-6) \tag{2.27}$$

it can be shown (41) that the kinetic energy can be expressed as

$$2T = \dot{\underline{R}}'\underline{G}^{-1}\ \dot{\underline{R}} = \sum_{i,j=1}^{3N-6} (G^{-1})_{ij}\dot{R}_i\dot{R}_j \tag{2.28}$$

where $\dot{\underline{R}}$ is the internal coordinate velocities and $\underline{G}^{-1}$ is the reciprocal of the $\underline{G}$ matrix.

The $\underline{G}$ matrix is defined as

$$\underline{G} = \underline{B}\,\underline{M}^{-1}\,\underline{B}' \tag{2.29}$$

where $\underline{B}$ is defined in equation (2.22) and $\underline{M}^{-1}$ is a diagonal matrix whose components are μ_i, where μ_i is the reduced mass.

If normal coordinates Q_k ($k = 1, 2, \ldots, 3N$) are introduced, the kinetic and potential energies achieve a simplier form. The normal coordinates are defined as linear combinations of mass-weighted Cartesian coordinates, $q_i = \sqrt{m_i}\, x_i$, as

$$Q_k = \sum_{i=1}^{3N} l_{ik} q_i \tag{2.30}$$

The coefficients, l_{ik}, are chosen so that the kinetic and potential energies have the form

$$2T = \sum_{k=1}^{3N} \dot{Q}_k^2 \qquad\qquad 2V = \sum_{k=1}^{3N} \lambda_k Q_k^2 \tag{2.31}$$

where λ_k are constants, i.e., the potential energy has no cross terms. A further property of normal coordinates is that the transformation from Cartesian coordinates to normal coordinates is orthogonal, i.e.,

$$\sum_{i=1}^{3N} \dot{q}_i^2 = \sum_{k}^{3N} \dot{Q}_k^2 \tag{2.32}$$

Newton's equations of motion are given by

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{Q}_k} + \frac{\partial V}{\partial Q_k} = 0 \ (k = 1, 2, \ldots, 3N) \tag{2.33}$$

If equations (2.31) are substituted into equation (2.33) the equations of motion are given by

$$\ddot{Q}_k + \lambda_k Q_k = 0 \qquad (2.34)$$

Equation (2.34) has the solutions:

$$Q_k = Q_k^{\circ} \cos(\lambda_k^{1/2} t + \varepsilon_k) \qquad (2.35)$$

where Q_k° and ε_k are the amplitude and phase constants, respectively, and λ_k is related to the frequency of the ith vibration by

$$\nu_i = \frac{(\lambda_k)^{1/2}}{2\pi c} \quad \text{where } i = k \qquad (2.36)$$

The normal coordinates are linearly related to the internal coordinates by the transformation $\underline{L}$, which diagonalizes $\underline{G}$ and $\underline{F}$, by

$$R_i = \sum_{i=1}^{3N-6} L_{ik} Q_k \quad (k = 1, 2, \ldots, 3N) \qquad (2.37)$$

or

$$\underline{R} = \underline{L}\,\underline{Q} \text{ or } \underline{Q} = \underline{L}^{-1}\underline{R} \qquad (2.38)$$

From equations (2.28) and (2.25) the kinetic and potential energies are expressed by

$$2T = \underline{\dot{Q}}'\,\underline{L}'\,\underline{G}^{-1}\,\underline{L}\,\underline{\dot{Q}} = \underline{\dot{Q}}'\,\underline{E}\,\underline{\dot{Q}} \qquad (2.39)$$

and

$$2V = \underline{Q}'\,\underline{L}'\,\underline{F}\,\underline{L}\,\underline{Q} = \underline{Q}'\,\underline{\Lambda}\,\underline{Q} \qquad (2.40)$$

where $\underline{\Lambda}$ is a diagonal matrix, with $\Lambda_{ii} = \lambda_i$, while $\underline{E}$ is a unit matrix. Therefore from equations (2.39) and (2.40)

$$\underline{L}' \underline{G}^{-1} \underline{L} = \underline{E} \tag{2.41}$$

and

$$\underline{L}' \underline{F} \underline{L} = \underline{\Lambda} \tag{2.42}$$

Solving for $\underline{L}'$ in equation (2.41) ($\underline{L}' = \underline{L}^{-1} \underline{G}$) and substituting for $\underline{L}'$ in equation (2.42)

$$\underline{G} \underline{F} \underline{L} = \underline{L} \underline{\Lambda} \tag{2.43}$$

or

$$|\underline{G} \underline{F} - \underline{E}\lambda_k| \underline{L} = 0 \tag{2.44}$$

or

$$\sum_{j}^{3N-6} \left(\sum_{p}^{3N-6} G_{ip} F_{pj} - \delta_{ij}\lambda_k \right) L_{jk} = 0 \tag{2.45}$$

where δ_{ij} is the Kronecker delta symbol. For equation (2.45) to be true

$$\sum_{p}^{3N-6} G_{ip} F_{pj} - \delta_{ij}\lambda_k = 0 \tag{2.46}$$

or

$$|\underline{G} \underline{F} - \underline{E}\lambda_k| = 0 \tag{2.47}$$

From equation (2.47) the eigenvalues for a particular molecule can be calculated. Equation (2.47) has 3N-6 nonzero roots.

The secular equation (2.47) may be further simplified by introducing the symmetry properties of the molecule.

The internal coordinates, R_i, can be transformed to symmetry coordinates, S_i, by use of an orthogonal matrix, $\underline{U}$:

$$\underline{S} = \underline{U}\ \underline{R} \qquad (2.48)$$

Recalling equation (2.38)

$$\underline{S} = \underline{U}\ \underline{L}\ \underline{Q} = \underline{L}_s\ \underline{Q} \qquad (2.49)$$

and
$$\underline{Q} = \underline{L}^{-1}\ \underline{U}^{-1}\ \underline{U}\ \underline{R} = \underline{L}_s^{-1}\ \underline{S} \qquad (2.50)$$

where $\underline{L}_s = \underline{U}\ \underline{L}$. The kinetic and potential energies, expressed in symmetry coordinates, are

$$2V = \underline{U}'^{-1}\ \underline{S}'\ \underline{F}\ \underline{U}^{-1}\ \underline{S} = \underline{U}\ \underline{S}'\ \underline{F}\ \underline{U}'\ \underline{S} \qquad (2.51)$$

and
$$2T = \underline{U}'^{-1}\ \dot{\underline{S}}'\ \underline{G}^{-1}\ \underline{U}^{-1}\ \dot{\underline{S}} = \underline{U}\ \dot{\underline{S}}'\ \underline{G}^{-1}\ \underline{U}'\ \dot{\underline{S}} \qquad (2.52)$$

where $\underline{U}^{-1} = \underline{U}'$ for an orthogonal matrix.

Equations (2.39) and (2.40) become

$$2T = \dot{\underline{Q}}'\ \underline{L}_s\ \underline{G}^{-1}\ \underline{L}_s'\ \dot{\underline{Q}} = \dot{\underline{Q}}'\ \underline{E}\ \dot{\underline{Q}} \qquad (2.53)$$

$$2V = \underline{Q}'\ \underline{L}_s\ \underline{F}\ \underline{L}_s'\ \underline{Q} = \underline{Q}'\ \underline{\Lambda}\ \underline{Q} \qquad (2.54)$$

Therefore from equations (2.53) and (2.54)

$$\underline{L}_s\ \underline{G}^{-1}\underline{L}_s' = \underline{E} = \underline{L}\ \underline{G}_s^{-1}\ \underline{L}' \qquad (2.55)$$

and
$$\underline{L}_s \underline{F} \underline{L}'_s = \underline{\Lambda} = \underline{L} \underline{F}_s \underline{L}' \qquad (2.56)$$

where
$$\underline{G}_s^{-1} = \underline{U} \underline{G}^{-1} \underline{U}' \qquad (2.57)$$

and
$$\underline{F}_s = \underline{U} \underline{F} \underline{U}' \qquad (2.58)$$

Thus equation (2.43) becomes

$$\underline{G}_s \underline{F}_s \underline{L} = \underline{L} \underline{\Lambda} \qquad (2.59)$$

or
$$|\underline{G}_s \underline{F}_s - \underline{E}\lambda_k| = 0 \qquad (2.60)$$

The $\underline{G}$ and $\underline{F}$ matrices are symmetrized and the secular equation is reduced to block form which simplifies the solution for the vibrational frequencies of the normal modes of vibration.

To make vibrational assignments one must examine the extent of displacement of the coordinates, x_i, y_i, and z_i. Once the solutions of the secular equation are obtained, the transformation matrix, $\underline{L}$, can be calculated from equation (2.44). The transformation matrix, $\underline{L}$, is related to the normal coordinates matrix, $\underline{Q}$, by

$$\underline{Q} = \underline{L}^{-1} \underline{R} \qquad (2.38)$$

From equation (2.22)

$$\underline{Q} = (\underline{L}^{-1} \underline{B})\underline{X} \qquad (2.61)$$

where $\underline{X}$ is a column matrix containing the displacement coordinates x_1, y_1, z_1, x_2, y_2, z_2, ..., x_n, y_n, z_n and $\underline{L}^{-1}$ is defined as the eigenvector inverse matrix. By plotting the displacements for each eigenvalue, λ_k, it is possible to determine which atom or atoms are changing for a particular vibration.

III. Experimental

Reagent grade chemicals were used throughout this investigation.

A. Purification of Solvents

Reagent grade diethylether (Et_2O) and tetrahydrofuran (THF) were purified by being refluxed with lithium aluminum hydride under prepurified nitrogen and were distilled. The fractions boiling at 34.5°C. and 65°C., respectively, were collected and stored under nitrogen and over sodium metal in sealed vessels.

Reagent grade acetone was purified by allowing the solvent to stand over anhydrous calcium chloride for at least three weeks. The acetone was subsequently refluxed with Drierite and distilled under nitrogen directly into the filtration flask.

B. Preparation of Tetrazoles and Related Chemicals

Hydrazoic Acid: The method of Garbrecht (43) was used. To a sludge of 520 g. of sodium azide and 500 ml. of water in 1500 ml. of toluene were added dropwise with stirring 250 ml. of concentrated sulfuric acid at 0°C. The toluene layer was decanted into a tightly stoppered bottle. Anhydrous sodium sulfate was used to dry the hydrazoic acid. The concentration of hydrazoic acid in toluene was determined by titration with standard sodium hydroxide and phenolthalein as the indicator.

N-cyclohexylformamide: The method of preparation described Ugi *et al.*, (44) was used. Ethyl formate was added dropwise to a slight excess of freshly distilled cyclohexylamine immersed in an ice bath. After the exothermic reaction ceased, the solution was refluxed for two hours and distilled to remove water, ethanol and unreacted cyclohexylamine. The N-cyclohexylformamide fraction was collected at 145-146°C. and 29 torr.

1-methyltetrazole: The preparation of methyl isocyanide of Ugi and Meyr (45) was utilized with a modification by Gilbert (26). To 0.6 moles of reagent grade N-methylformamide in 100 ml. of pyridine and 200 ml. of chloroform were added dropwise with stirring 0.3 moles of phosphorous oxytrichloride at 0°C. The reaction was allowed to proceed at 0°C. for one-half hour after the addition of phosphorous oxytrichloride. The methyl isocyanide, chloroform mixture was distilled with a minimum pot temperature (in order to prevent polymerization of methyl isocyanide) into a solution of excess hydrazoic acid in toluene. Separation of pyridine from the methyl isocyanide, chloroform fraction was best obtained by distillation through a 24 inch fractionating column packed with glass helices. The distillate and hydrazoic acid in toluene were allowed to reflux for twenty-four hours under anhydrous conditions. Evaporation to dryness with an air jet gave a crude product of approximately twenty to thirty per cent yield. Sublimation of the crude product under reduced pressure gave a white, crystalline product whose melting point was 37-38°C. The infrared spectrum of 1-methyltetrazole is given in Table I. If large quantities of the reactants are used, the per cent yield of 1-methyltetrazole decreases because of the increased methyl isocyanide polymerization which is

Table I. Infrared Spectrum[a] of 1-methyltetrazole from 100 to 5000 cm^{-1}.

3400 (vw) broad

3135 (s)

2980 (m)

1639 (vw)

1496 (s)

1471 (vw)

1422 (m)

1402 (w)

1279 (s)

1225 (m)

1174 (vs)

1113 (s)

1058 (m)

1040 (w)

973 (vs)

928 (m)

881 (vs)

719 (s)

678 (vs)

658 (s)

534 (s)

476 (s)

357 (s)

---

[a] Intensities in parenthesis (vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder).

catalyzed by pyridine and heat. Even with the use of a glass helices column, the separation of the pyrdine and methyl isocyanide is not complete. Since pyridine appears to prevent the initial precipitation of 1-methyltetrazole, quinoline and aniline were substituted for pyridine as bases in the preparation of methyl isocyanide. Quinoline and aniline are of comparable basicity to pyridine, but have higher boiling points. With quinoline and aniline no methyl isocyanide could be produced.

<u>1-phenyltetrazole</u>: The method of Herbst and Fallon (46) was used. To 0.25 moles of formanilide in toluene were added dropwise with stirring 0.25 moles of phosphorous pentachloride at 0°C. Upon complete reaction excess hydrazoic acid in toluene was added to the solution. After being refluxed for twenty-four hours, the solution was poured over ice, made alkaline with sodium hydroxide and filtered. The residue was washed first with a 4% sodium hydroxide solution and then with water. A further quantity was obtained by separating the toluene layer from the initial filtrate and evaporating it to dryness. Sublimation of the crude product at reduced pressure gave a white crystalline solid which melted at 65-66°C. The infrared spectrum of 1-phenyltetrazole is presented in Table II.

<u>1-cyclohexyltetrazole</u>: The preparation by Ugi <u>et al</u>., (44) of cyclohexyl isocyanide was utilized. To a solution consisting of 0.5 moles of N-cyclohexylformamide, 250 ml. of pyridine and 200 ml. of petroleum ether (b.p. 30-60°C.), 0.3 moles of $POCl_3$ were added dropwise with

Table II. Infrared Spectrum[a] of 1-phenyltetrazole from 100-5000 cm^{-1}.

3125 (vs)	1100 (s)
1618 (vs)	1085 (m)
1510 (vs)	1058 (m)
1471 (s)	1000 (s)
1400 (s)	967 (s)
1380 (sh)	916 (s)
1340 (w)	888 (s)
1310 (w)	765 (vs)
1284 (w)	718 (s)
1240 (vw)	688 (vs)
1218 (vs)	504 (s)
1198 (w)	441 (s)
1180 (w)	355 (s)
1170 (vw)	295 (s)
	177 (s)

---

[a] As defined in Table I.

stirring at 0°C. After the addition of $POCl_3$ was complete, 300 ml. of ice water was added with stirring until all of the solid material had dissolved. The organic layer was separated from the aqueous layer. The aqueous layer was extracted with three-20 ml. portions of petroleum ether and the extract was added to the organic layer which was extracted with three-25 ml. portions of water and dried over magnesium sulfate. The crude product in petroleum ether was added to an excess of hydrazoic acid in toluene. The mixture was allowed to reflux for twenty-four hours after which the solvent was removed by evaporation in an air jet. An oily solution remained. To this solution was added about 20 ml. of acetone. Immediately, crude, pale-yellow 1-cyclohexyltetrazole precipitated and was sublimed at reduced pressure to yield a white, very fluffy crystalline compound which melted at 46-47°C. The infrared spectrum is given in Table III.

Tetrazole: Tetrazole was donated by Dr. N. A. Daugherty and was prepared by diazotization of 5-aminotetrazole. The infrared spectrum of tetrazole is presented in Table IV.

Sodium Tetrazolate Monohydrate: Equimolar amounts of sodium hydroxide and tetrazole were mixed in water. Sodium tetrazolate monohydrate was crystallized by slow evaporation of the aqueous solution. To remove unreacted tetrazole, ethyl acetate was added to the sodium tetrazolate monohydrate crystals and filtered. Sodium tetrazolate monohydrate was recrystallized from water. The infrared and Raman spectra are presented in Tables V and VI.

Table III. Infrared Spectrum[a] of 1-cyclohexyltetrazole from 100-5000 cm^{-1}.

3125 (s)	1101 (vs)
2930 (vs)	1054 (m)
2850 (s)	1032 (m)
2650 (w)	1001 (s)
1740 (vw)	970 (s)
1610 (vw)	920 (vw)
1470 (s)	897 (vs)
1450 (vs)	881 (vs)
1424 (m)	820 (s)
1404 (w)	746 (s)
1366 (m)	718 (vw)
1344 (w)	675 (vs)
1310 (m)	659 (vs)
1266 (m)	554 (m)
1242 (w)	468 (m)
1180 (sh)	439 (s)
1167 (vs)	337 (m)
1138 (s)	242 (m)

[a] As defined in Table I.

Table IV. Infrared Spectrum[a] of Tetrazole from 300-5000 cm^{-1}.

3140 (m)
2930 (m)
2350 (vw)
1800 (m)
1665 (m)
1522 (m)
1455 (m)
1445 (m)
1258 (vs)
1152 (s)
1082 (m)
1052 (m)
1018 (m)
980 (w)
950 (vw)
920 (w)
780 (vw)
665 (vs)
659 (s)
557 (s)
451 (s)

---

[a] As defined in Table I.

Table V. Infrared Spectrum[a] of Sodium Tetrazolate Monohydrate from 300-5000 cm^{-1}.

3300 (vs)
3120 (sh)
2930 (m)
2370 (m)
1785 (m)
1685 (s)
1640 (sh)
1455 (s)
1445 (s)
1290 (s)
1210 (s)
1161 (vs)
1132 (m)
1065 (vs)
1023 (vs)
1015 (vs)
910 (vs)
702 (vs)
660 (w)
454 (w)

---

[a] As defined in Table I.

Table VI. Raman Spectrum[a] of Sodium Tetrazolate Monohydrate from 150-5000 cm^{-1}.

3128	(m)
1780	(vw)
1696	(sh)
1647	(s)
1438	(s)
1287	(vs)
1189	(vs)
1130	(w)
1079	(w)
1025	(w)
1009	(w)
702	(w)

[a] As defined in Table I.

C. Preparation of Metal Compound Reactants

Nickel(II) chloride: To hydrated nickel(II) chloride was added an excess of thionyl chloride (47). The mixture was stirred until the effervescence of sulfur dioxide and hydrogen chloride ceased and was left to stand for one-half hour under nitrogen. The excess thionyl chloride was removed by distillation under reduced pressure.

Addition of nitrogen to the reaction vessel permitted the system to attain atmospheric pressure under anhydrous conditions. The yellow, scale-like nickel(II) chloride was stored under anhydrous conditions.

Iron(II) chloride: Anhydrous iron(III) chloride was prepared by the same method as described for anhydrous nickel(II) chloride with the exception that the mixture was refluxed for two hours after the addition of excess thionyl chloride.

Anhydrous iron (II) chloride was prepared with the method described by Kovacic and Brace (48). To 1 mole of anhydrous iron(III) chloride under anhydrous conditions was added 2 moles of chlorobenzene. The mixture was stirred at a rapid rate and heated for thirty minutes to 126°C., whereupon the black slurry thickened. The reaction was allowed to proceed for two hours at 128° to 139°C. In the course of the reaction the mixture became light tan, less viscous and hydrogen chloride gas was evolved. The tan solid was filtered under anhydrous conditions, washed repeatedly with chloroform, and dried *in vacuo*. The iron(II) chloride was stored under anhydrous conditions.

Dichlorobis(triethylphosphine)nickel(II): The method described by Jensen *et al.*, (49) was used. Triethylphosphine (prepared by the reaction of an equimolar amount of phosphorous trichloride and ethyl magnesium bromide) was added to an equimolar amount of a cold ethanolic solution of hydrated nickel chloride. Wine-red, crystalline dichlorobis(triethylphosphine)nickel(II) precipitated and was immediately filtered. The compound was purified by dissolving the complex in benzene and was recrystallized by the addition of pentane. The infrared spectrum is given in Table VII and was used to identify the dichlorobis(triethylphosphine)nickel(II).

D. Preparation of Compounds.

Bis(tetrazolato)copper(II)monohydrate: To 0.02 moles of tetrazole in 50 ml. of water were added dropwise with stirring 0.0095 moles of copper(II) nitrate trihydrate in 50 ml. of water. Immediately a pale-blue solid precipitated. The solution was stirred for four hours, filtered and washed repeatedly with water, ethylacetate, ethanol and ether to remove any remaining reactants. A yield of eighty-two per cent was obtained. *Anal.* Calculated for $Cu(CHN_4)_2 \cdot H_2O$: Cu, 28.93; C, 10.94; H, 1.84; N, 51.02. Found: Cu, 28.95; C, 11.04; H, 1.83; N, 51.15.

1-methyl-5-tetrazolyllithium·1/2 THF: To an excess of *n*-butyllithium (prepared by the reaction of equimolar amounts of lithium and *n*-butylchloride at -35°C. under nitrogen) in 300 ml. of freshly distilled, anhydrous THF were added 0.02 moles of 1-methyltetrazole under anhydrous

Table VII. Infrared Spectrum of Dichlorobis-(triethylphosphine)nickel(II) from 650-5000 cm^{-1}.

3390 (m)[a]
2910 (vs)
2880 (s)
2820 (m)
2450 (w)
1665 (m)
1595 (m)
1560 (vs)
1482 (m)
1462 (m)
1445 (m)
1408 (s)
1380 (vs)
1375 (sh)
1281 (vs)
1147 (sh)
1142 (m)
1138 (sh)
1085 (m)
1068 (m)
1036 (vs)
1030 (sh)
1009 (w)
999 (m)
985 (vw)
890 (vw)
857 (s)
813 (vs)
790 (vw)
760 (vs)
718 (vs)
702 (s)
689 (s)

---

[a] As defined in Table I.

conditions at -50°C. The solution was stirred continuously for one hour at -50°C. after which a white solid precipitated. If the solution was warmed, butane was evolved, as verified by mass spectrography. The solid was filtered under anhydrous conditions and washed repeatedly with anhydrous THF and Et_2O to remove unreacted 1-methyltetrazcle. Anal. Calculated for $LiC_2H_3N_4 \cdot 1/2$ THF: C, 38.11; H, 5.60; N, 44.44. Found: C, 38.62; H, 4.92; N, 45.06.

Bis(1-methyl-5-tetrazolyl)nickel(II): 1-methyl-5-tetrazolyllithium·1/2THF was prepared as above but was used in situ. To about 0.02 moles of a THF suspension of the tetrazolyllithium at about -50°C. were added about 0.01 moles of dichlorobis(triethylphosphine)nickel(II). The mixture was stirred for two hours under nitrogen and was allowed to come to room temperature under nitrogen and stand for about four hours. A finely divided green solid was separated either by centrifugation or by filtration under anhydrous and anaeorobic conditions, washed repeatedly with anhydrous acetone, THF, and Et_2O, allowed to dry in and stored under an inert atmosphere. A yield of eighty per cent (based on the amount of dichlorobis(triethylphosphine)-nickel(II)) was obtained. A very low yield was obtained when anhydrous nickel(II) chloride was used in place of the triethylphosphine complex even after being stirred at room temperature for one week. Extreme care must be exercised to insure that the complex is not exposed to air or moisture when wet. When wet the complex decomposes to give a yellow complex, whereas, when dry the decomposition rate appears to be much slower and without the formation of the yellow compound. No attempt was made to identify the yellow compound. Anal. Calculated for $Ni(C_2H_3N_4)_2$: Ni, 26.11; CN, 23.14. Found: Ni, 26.00; CN, 22.97. Satisfactory commercial C, H, and N analyses could not be obtained. If the complex is treated with nitromethane, a new green substance forms which appears to be a disolvate. Anal. Calculated for $Ni(C_2H_3N_4)_2 \cdot 2CH_3NO_2$: Ni, 16.9. Found: Ni, 17.1.

Bis(1-cyclohexyl-5-tetrazolyl)nickel(II): The same procedure was used as described for $Ni(C_2H_3N_4)_2$ except that the solution and suspended solid were allowed to stand for 1 to 2 days before filtration of the light green complex. When wet and exposed to air, the compound decomposes to give a yellow compound. As was observed for $Ni(C_2H_3N_4)_2$ the decomposition is much slower when the sample is dry. Anal. Calculated for $Ni(C_7H_{11}N_4)_2$: Ni, 16.26; CN, 14.41; C, 46.57; H, 6.14. Found: Ni, 16.23; CN, 14.29; C, 46.18; H, 6.81. The commercial nitrogen analysis was not satisfactory.

Attempted Preparation of bis(1-phenyl-5-tetrazolyl)nickel(II): When the same conditions and method as described for bis(1-methyl-5-tetrazolyl)nickel(II) were used no reaction occurred between 1-phenyl-5-tetrazolyllithium and dichlorobis(triethylphosphine)nickel(II) even when the THF solution and suspension of 1-phenyl-5-tetrazolyllithium were heated for one week. Filtration of the solution and suspension left only the white 1-phenyl-5-tetrazolyllithium.

Attempted Preparation of bis(1-methyl-5-tetrazolyl)iron(II): To a 0.02 moles suspension of 1-methyl-5-tetrazolyllithium was added 0.01 moles of anhydrous iron(II) chloride. After letting the suspension stand for 6 weeks a very poorly defined orange compound was isolated. Anal. Calculated for $Fe(C_2H_3N_4)_2$: Fe, 25.17. Found: 26.50. Because of the length of time required for preparation and lack of purity, this attempted preparation was abandoned.

E. Analytical Methods

Nickel Determination

The following two methods were used.

Volumetric: Since cyanide ion is formed from the decomposition of bis(1-substituted-5-tetrazolyl)nickel(II) complexes with ammonia (see Results), the standard volumetric technique for the determination of nickel with cyanide ion (50) could not be used. To a weighed sample of the complex (about 50-80 mg.) was added 30 ml. of 6 M hydrochloric acid and 50 ml. of water. The solution was heated to boiling to expel hydrogen cyanide and was evaporated to partial dryness. To the residue (nickel(II) chloride) was added 20 ml. of 1 M sulfuric acid. The solution was neutralized with concentrated ammonium hydroxide to which were added 5 ml. of concentrated ammonium hydroxide, 30 ml. of water, 20 ml. of a standard cyanide ion solution and 1 ml. of potassium iodide (1 g. per 100 ml.) as the indicator. The uncomplexed cyanide ion was titrated with a standard silver ion solution.

Gravimetric: A weighed amount of sample was placed in a tared crucible and heated slowly to decompose the complex to nickel(II) oxide and the crucible was heated to constant weight.

Iron Determination

To approximately 100 mg. of sample was added 20 ml. of concentrated nitric acid. The mixture was diluted to 75 ml. after dissolution of the sample. Two to three drops of methyl orange and 6 M aqueous ammonia were added until the solution was basic. After coagulation the iron(III) hydroxide was filtered with No. 540 filter paper, washed several times and placed in a tared crucible which was heated to constant weight. The iron in the sample was determined as iron(III) oxide.

Copper Determination

The percentage of copper was determined spectrophotometrically. To duplicate samples of 20 to 40 mg. of sample 5 ml. of concentrated nitric acid was added. After the complex dissolved, 30 ml. of water was added and most of the nitric acid was fumed away. The solutions were cooled, diluted with a small amount of water and quantitatively transferred to 25 ml. volumetric flasks. Ten ml. of a buffer which was 5.0 M with respect to both ammonia and ammonium chloride was added to the flasks. The samples were diluted to volume with water and their absorbancies were measured at 620 mμ with a Beckmann model DU spectrophotometer.

Each time that a copper analysis was made, two or more samples of known composition were also run.

Cyanide Determination

Since cyanide ion is formed quantitatively by the decomposition of bis(1-substituted-5-tetrazolyl)nickel(II) complexes with ammonia (see Results), it is possible to determine the amount of tetrazole present once the percentage of nickel is known. To 40-60 mg. of sample were added 5 ml. of concentrated ammonium hydroxide, 30 ml. of water, 1 ml. of potassium iodide solution and 20 ml. of standard cyanide ion solution. The uncomplexed cyanide ion was titrated with standard silver ion from which the amount of cyanide ion, which is present as a result of decomposition of the complex, can be calculated.

Carbon, Hydrogen and Nitrogen Analyses

The Spang Microanalytical Laboratory, Ann Arbor, Michigan determined carbon, hydrogen and nitrogen.

F. Purification of Nitrogen Gas

Matheson prepurified nitrogen was passed through a train of sulfuric acid, barium oxide and phosphorous pentoxide to remove any water vapor and through a column of copper wire at 500°C. and a column of Kieselguhr at 170°C. to remove any oxygen.

G. Spectroscopic Techniques

Infrared spectra were recorded on Unicam, S.P. 200 spectrometer with potassium bromide discs or with Nujol and Fluorolube mulls between sodium chloride plates for the 650-5000 cm^{-1} region. For the 100-650 cm^{-1} region a Perkin-Elmer Model 301 spectrometer was used. Spectra were obtained with Nujol mulls between cesium bromide or polyethylene plates. Below 300 cm^{-1} polyethylene plates were used exclusively. Care was taken to avoid contact with water vapor.

The unpolarized and polarized Raman spectra for a 1 M and a 3 M aqueous solutions of sodium tetrazolate monohydrate were obtained, respectively, with a helical Toronto arc as the source of exciting radiation. The spectrograph was a Gaertner two-prism spectrograph with a f3.5 camera lens. The 22938 cm^{-1} line of mercury was effectively isolated from the mercury emission spectrum by a saturated aqueous solution of potassium nitrite to absorb the ultraviolet lines and an ethyl violet-ethanol solution to filter out light of longer wavelength than the blue exciting line. The spectrograph was adjusted to give a dispersion of about 200 cm^{-1} per mm on the plate with a resolution of about 10-15 cm^{-1}. The spectra were recorded on Eastmann Kodak IIa-o spectroscopic plates preheated in vacuum for twelve hours.

The spectral lines on the photographic plates were measured directly with a Mann comparator and indirectly from tracings by using a traveling scale. The tracings were obtained with a Joyce-Lockel microdensitometer. The values of the peaks in cm^{-1} were calculated by a computer program with an interpolation from a quartic equation.

The reflectance electronic absorption spectra were measured with a DK2 spectrometer and diffuse reflectance attachment and a Cary Model 15 spectrometer with reflectance attachment. For the measurements with the Cary 15 finely divided undiluted samples were placed between quartz plates with one of the plates covered with electrical tape. A 2" x 2" aluminum plate with a cylindrical bore (1" x 1/16") was used as a sample holder for the DK2 measurements. All samples were prepared with two parts of magnesium oxide or silica to one part of sample. The samples were packed with force into the sample holder so that none of the sample would fall into the reflectance cavity. For the water sensitive complexes the samples were loaded in a dry box and kept under anhydrous conditions until the spectra were obtained. During scanning the samples were exposed to the atmosphere. Each spectrum was repeated to determine whether or not decomposition had taken place. In all cases no observable decomposition occurred.

H. Magnetic Susceptibility Measurements

The Gouy method was used to obtain the magnetic moments for the paramagnetic compounds. An Alpha Scientific Laboratories AL 7500 M Electromagnet and AL 7500 PS Power Supply equipped with a Mettler single pan balance was used and an inert atmosphere was used for moisture sensitive compounds.

IV. Vibrational Analysis Calculation (Normal Coordinate Analysis)

The normal coordinate analysis calculation was performed on the Control Data 3600 Computer of the Michigan State University Computer Laboratory. The Fortran program, SD-9032I, written by Schachtschneider (51,52) and modified by Dr. L. B. Sims and Mr. Hans Sachse, was used to calculate the eigenvalues for the genuine normal modes of vibration for sodium tetrazolate.

The program SD-9032I requires the following input data:

(a) The atomic positions (polar coordinates).

(b) The internal coordinates (bond stretching, valence angle bending, out-of-plane wagging, torsional, linear valence angle bending, and in-plane wagging).

(c) A potential field of the <u>generalized</u> <u>valence</u> <u>force</u> <u>field</u> type (GVFF).

(d) Masses of the atoms.

(e) The $\underline{U}$ matrix (symmetry properties of the molecule).

The $\underline{G}$ matrix is calculated from the equation

$$\underline{G} = \underline{B}' \, \underline{M}^{-1} \, \underline{B} \tag{4.1}$$

where $\underline{M}^{-1}$ is the diagonal matrix of the reciprocal atomic masses, and $\underline{B}$ is the transformation from Cartesian displacement coordinates $\underline{X}$ to the internal coordinates $\underline{R}$:

$$\underline{R} = \underline{B} \, \underline{X} \tag{4.2}$$

The matrix elements are computed by the Wilson $\bar{s}$-vector technique (30). The displacements of the atoms are described by a vector,

$\bar{\rho}_a$, one for each atom, so that the internal coordinates are expressed by

$$R_t = \sum_{a=1}^{N} \bar{s}_{ta} \cdot \bar{\rho}_a = \sum_{i=1}^{3N} B_{ti} x_i \quad (t=1,2,\ldots,3N-6) \tag{4.3}$$

where $\bar{s}_{ta}$ is the vector which describes the displacement of atom a and $\bar{\rho}_a$ is the unit displacement vector of atom a. The three B_{ti}'s which belong to atom a are the components of the vector $\bar{s}_{ta}$.

The $\bar{s}$-vectors are computed by use of Wilson's formulae (30) which are given in Table VIII for the various internal coordinates. The unit vector, $\bar{e}_{ij}$, is given by

$$\bar{e}_{ij} = [(x_j-x_i)\bar{i} + (y_j-y_i)\bar{j} + (z_j-z_i)\bar{k}]/r_{ij} \tag{4.4}$$

where r_{ij} is the bond distance between atoms i and j and $\bar{i}$, $\bar{j}$, and $\bar{k}$ are the unit vectors in the x, y, and z directions.

The solution of the secular equation (see Section II-B):

$$\underline{G}\,\underline{F}\,\underline{L} = \underline{L}\,\underline{\Lambda} \tag{4.5}$$

is obtained by diagonalizing the product $\underline{G}\,\underline{F}$ by use of the Jacobi method for symmetric matrices (53). Although $\underline{G}\,\underline{F}$ is not symmetric, the solution may be accomplished by solving two symmetric problems (50).

The $\underline{G}\,\underline{F}$ problem is solved in two stages. First, consider the solution of

$$\underline{G}\,\underline{D} = \underline{D}\,\underline{\Gamma} \tag{4.6}$$

where $\underline{D}$ is the eigenvector matrix and $\underline{\Gamma}$ is the diagonal eigenvalue

Table VIII. Formulae for the Computation of $\bar{s}_{ta}$.

Bond Stretch

$$\bar{s}_{ti} = -\bar{e}_{ij}$$

$$\bar{s}_{tj} = \bar{e}_{ij}$$

Valence Angle Bend for Angle α_{ijl}

$$\bar{s}_{ti} = \frac{\cos \alpha_{ijl}\bar{e}_{li} - \bar{e}_{lj}}{r_{li}\sin_{ijl}}$$

$$\bar{s}_{tj} = \frac{\cos\alpha_{ijl}\bar{e}_{lj} - \bar{e}_{li}}{r_{lj}\sin\alpha_{ijl}}$$

$$\bar{s}_{tk} = \frac{(r_{li} - r_{lj}\cos\alpha_{ijl})\bar{e}_{li} + (r_{lj} + r_{li}\cos\alpha_{ijl})\bar{e}_{lj}}{r_{li}r_{lj}\sin\alpha_{ijl}}$$

Out-of-plane Wag γ_{mijl}, For Coplanar Atoms

$$s_{ti} = -\frac{1}{r_{mi}} - \frac{\sin\alpha_{lij}}{r_{ij}\sin\alpha_{mil}} - \frac{\sin\alpha_{mij}}{r_{il}\sin\alpha_{lij}}$$ "apex atom"

$$s_{tj} = \frac{\sin\alpha_{mil}}{r_{ij}\sin\alpha_{jil}}$$ "anchor atom"

$$s_{tl} = \frac{\sin\alpha_{mij}}{r_{il}\sin\alpha_{jil}}$$ "anchor atom"

$$s_{tm} = \frac{1}{r_{im}}$$ "end atom"

Table VIII. (continued).

Torsion δ_{ijlm}

$$\bar{s}_{ti} = \frac{-\bar{e}_{ij} \times \bar{e}_{jl}}{r_{ij} \sin^2\alpha_{ijl}}$$

$$\bar{s}_{tj} = \frac{(r_{jl} - r_{ij}\cos\alpha_{ijl})\bar{e}_{ij} \times \bar{e}_{jl}}{r_{jl} r_{ij} \sin\alpha_{ijl} \sin\alpha_{kjl}} - \frac{\cos\alpha_{jlm} \bar{e}_{ml} \times \bar{e}_{lj}}{r_{jl} \sin\alpha_{jlm} \sin\alpha_{jlm}}$$

$$\bar{s}_{tl} = \frac{(r_{lj} - r_{ml}\cos\alpha_{jlm})\bar{e}_{ml} \times \bar{e}_{lj}}{r_{lj} - r_{ml} \sin\alpha_{jlm}} - \frac{\cos\alpha_{ijl} \bar{e}_{ij} \times \bar{e}_{jl}}{r_{lj} \sin\alpha_{ijl} \sin\alpha_{ijl}}$$

$$\bar{s}_{tm} = \frac{-\bar{e}_{ml} \times \bar{e}_{lj}}{r_{ml} \sin^2\alpha_{jlm}}$$

matrix of $\underline{G}$. If there are redundancies present, $\underline{\Gamma}$ will contain a row and column with elements of zero for each redundancy. Thus $\underline{G}$ will give a zero root for each redundancy. Since $\underline{G}$ is real and symmetric, $\underline{D}$ is orthogonal and the roots are real and positive; thus;

$$\underline{G} = \underline{D}\,\underline{\Gamma}\,\underline{D}' \tag{4.7}$$

Let $\underline{W}$ be a matrix defined as

$$\underline{W} = \underline{\Gamma}^{1/2}\,\underline{D} \tag{4.8}$$

Then:

$$\underline{G} = \underline{W}\,\underline{W}' \tag{4.9}$$

By defining a matrix $\underline{H}$ as

$$\underline{H} = \underline{W}'\,\underline{F}\,\underline{W} \tag{4.10}$$

the secular equation (4.5) can be written as

$$\underline{H}\,\underline{C} = \underline{C}\,\underline{\Lambda} \tag{4.11}$$

where $\underline{C}$ is the orthogonal eigenvector matrix of $\underline{H}$ and $\underline{\Lambda}$ is the diagonal eigenvalue matrix of $\underline{H}$. The elements of $\underline{\Lambda}$ are the λ_i, which are related to the vibrational frequencies, ν_i, by:

$$\nu_i = \frac{(\lambda_i)^{1/2}}{2\pi c} \tag{4.12}$$

The eigenvector matrix $\underline{L}$ (see Section II-B) is given by

$$\underline{L} = \underline{W}\,\underline{C} \tag{4.13}$$

and its inverse by

$$\underline{L}^{-1} = \underline{C}^{-1}\ \underline{W}^{-1} \tag{4.14}$$

The Cartesian displacement coordinates from which it is possible to make the vibrational assignments are formulated by a transformation, $\underline{T}$, from normal coordinate space to Cartesian space.

$$\underline{X} = \underline{T}\ \underline{Q} \tag{4.15}$$

For each normal vibration, ν_i, there are associated three Cartesian displacements x_n, y_n, and z_n with each atom, a. The elements of column i of $\underline{T}$, taken three at a time, may be considered to be the elements of a vector $\overline{T}_i^a$ with its origin at atom a. These vectors give the direction of the straightline motions of the a atoms in normal mode i and the lengths show the relative amplitudes for each atom.

The transformation matrix, $\underline{T}$, is computed from the equation (50).

$$\underline{T} = \underline{M}^{-1}\ \underline{B}'\ \underline{F}\ \underline{L}\ \underline{\Lambda}^{-1} \tag{4.16}$$

where all of the matrices have already been defined.

The structure of sodium tetrazolate has been determined by Palenik (54) and is given in Table IX. The system contains nineteen internal coordinates: 6 bond stretching coordinates (Δr_{12}, Δr_{23}, Δr_{34}, Δr_{45}, Δr_{51}, Δr_{56}), 7 angle bending coordinates ($\Delta\alpha_{156}$, $\Delta\alpha_{456}$, $\Delta\alpha_{123}$, $\Delta\alpha_{234}$, $\Delta\alpha_{345}$, $\Delta\alpha_{451}$, $\Delta\alpha_{512}$), 1 out-of-plane wag ($\Delta\gamma_{6514}$), and 5 torsions ($\Delta\delta_{1234}$, $\Delta\delta_{2345}$, $\Delta\delta_{3451}$, $\Delta\delta_{4512}$, $\Delta\delta_{5123}$).

Table IX. Structure of Sodium Tetrazolate.

r_{12}[a] = r_{34} = 1.348 A°

r_{23} = 1.310 A°

r_{15} = r_{45} = 1.329 A°

r_{56} = 0.911 A°

$\angle_{456}$ = $\angle_{156}$ = 123.8°

$\angle_{154}$ = 112.4°

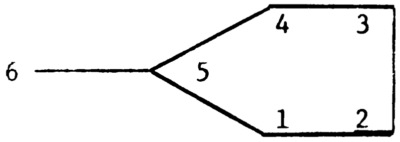
$\angle_{512}$ = $\angle_{345}$ = 104.3°

$\angle_{123}$ = $\angle_{234}$ = 109.5°

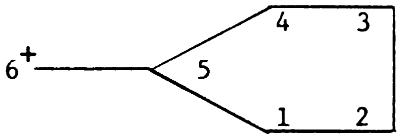
---

[a] The subscripts refer to the position of the atoms in the ring. See Historical Section for correct numbering of the ring. The number 6 refers to the hydrogen bonded to the carbon atom.

In Figure II the four atoms, 1,5,4, and 6, define a plane. For an out-of-plane wagging motion of the bond which is defined by atoms 5 and 6 the bond 5-6 is displaced out of the original plane (Figure III), where + in Figure III designates the out-of-plane motion.

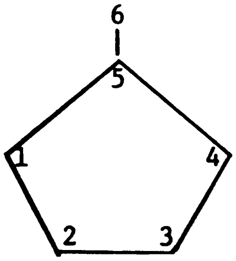


II

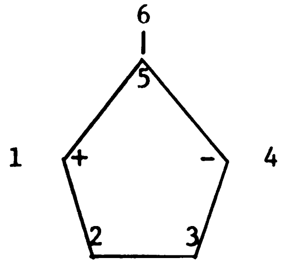


III

In Figure IV the fours atoms, 1,2,3, and 4, define a plane. For a torsional motion (Figure V) the bond defined by atoms 1 and 2 moves out of the original plane and the bond defined by atoms 3 and 4 moves out of the original plane but in the opposite direction.



IV



V

The potential field is of the GVFF type and contains both diagonal and off diagonal force constants.

$$
\begin{aligned}
2V &= f_{1,1}(\Delta r_1)^2 + f_{2,2}(\Delta r_2)^2 + f_{2,3}(\Delta r_2)(\Delta r_3) \\
&+ f_{2,4}(\Delta r_2)(\Delta r_4) + f_{2,5}(\Delta r_2)(\Delta r_5) + f_{2,6}(\Delta r_2)(\Delta r_6) \\
&+ f_{2,7}(\Delta r_2)(\Delta \alpha_7) + f_{2,8}(\Delta r_2)(\Delta \alpha_8) + f_{2,9}(\Delta r_2)(\Delta \alpha_9) \\
&+ f_{2,10}(\Delta r_2)(\Delta \alpha_{10}) + f_{3,3}(\Delta r_3)^2 + f_{3,4}(\Delta r_3)(\Delta r_4) \\
&+ f_{3,5}(\Delta r_3)(\Delta r_5) + f_{3,10}(\Delta r_3)(\Delta \alpha_{10}) + f_{3,11}(\Delta r_3)(\Delta \alpha_{11}) \\
&+ f_{4,4}(\Delta r_4)^2 + f_{4,5}(\Delta r_4)(\Delta r_5) + f_{4,6}(\Delta r_4)(\Delta r_6) + \\
&f_{4,11}(\Delta r_4)(\Delta \alpha_{11}) + f_{4,12}(\Delta r_4)(\Delta \alpha_{12}) + f_{5,5}(\Delta r_5)^2 \\
&+ f_{5,6}(\Delta r_5)(\Delta r_6) + f_{5,12}(\Delta r_5)(\Delta \alpha_{12}) + f_{5,13}(\Delta r_5)(\Delta \alpha_{13}) \\
&+ f_{6,6}(\Delta r_6)^2 + f_{6,7}(\Delta r_6)(\Delta \alpha_7) + f_{6,8}(\Delta r_6)(\Delta \alpha_8) \\
&+ f_{6,9}(\Delta r_6)(\Delta \alpha_9) + f_{6,13}(\Delta r_6)(\Delta \alpha_{13}) + f_{7,7}(\Delta \alpha_7)^2 \\
&+ f_{7,8}(\Delta \alpha_7)(\Delta \alpha_8) + f_{7,9}(\Delta \alpha_7)(\Delta \alpha_9) + f_{8,8}(\Delta \alpha_8)^2 \\
&+ f_{8,9}(\Delta \alpha_8)(\Delta \alpha_9) + f_{9,9}(\Delta \alpha_9)^2 + f_{9,10}(\Delta \alpha_9)(\Delta \alpha_{10}) \\
&+ f_{9,11}(\Delta \alpha_9)(\Delta \alpha_{11}) + f_{9,12}(\Delta \alpha_9)(\Delta \alpha_{12}) + f_{9,13}(\Delta \alpha_9)(\Delta \alpha_{13}) \\
&+ f_{10,10}(\Delta \alpha_{10})^2 + f_{10,11}(\Delta \alpha_{10})(\Delta \alpha_{11}) \\
&+ f_{10,12}(\Delta \alpha_{10})(\Delta \alpha_{12}) + f_{10,13}(\Delta \alpha_{10})(\Delta \alpha_{13}) \\
&+ f_{11,11}(\Delta \alpha_{11})^2 + f_{11,12}(\Delta \alpha_{11})(\Delta \alpha_{12}) + f_{12,12}(\Delta \alpha_{12})^2 \\
&+ f_{13,13}(\Delta \alpha_{13})^2 + f_{14,14}(\Delta \gamma_{14})^2 + f_{15,15}(\Delta \delta_{15})^2 \\
&+ f_{15,16}(\Delta \delta_{15})(\Delta \delta_{16}) + f_{15,19}(\Delta \delta_{15})(\Delta \delta_{19}) \\
&+ f_{16,16}(\Delta \delta_{16})^2 + f_{17,17}(\Delta \delta_{17})^2 + f_{18,18}(\Delta \delta_{18})^2 \\
&+ f_{19,19}(\Delta \delta_{19})^2.
\end{aligned}
\tag{4.17}
$$

The relationship between the subscripts and the internal coordinates is given in Table X.

The initial stretching force constants were approximated with Badger's rule (55,56,57) which has been improved by Herschbach (58) to give

$$F = \left(\frac{a_{ij} - d_{ij}}{r_e - d_{ij}}\right)^3 \tag{4.18}$$

where r_e is the equilibrium bond length, and a_{ij} and d_{ij} are constants which are fixed for bonds between atoms from rows i and j of the periodic table. The initial in-plane angle force constants were transferred from those for the cyclopentadienide ion (59) and those for the out-of-plane modes from benzene (60). These force constants were adjusted by trial and error until a reasonable fit was obtained between the calculated eigenvalues and the observed eigenvalues. The interaction force constants were added one at a time and varied over a reasonable range from negative to positive. The interaction constants which gave a closer convergence to the observed eigenvalues were retained in the potential field.

The symmetry of the tetrazolate ion is C_{2v}. The set of eighteen Cartesian displacement vectors for the tetrazolate ion reduces to $6A_1 + 2A_2 + 6B_1 + 4B_2$. Removal of the translational and rotational representations ($A_1 + A_2 + 2B_1 + 2B_2$) leaves $5A_1 + A_2 + 4B_1 + 2B_2$ representations for the genuine vibrational modes. The nature of the twelve vibrational modes may be further specified in terms of the contribution made by the internal coordinates, and are

Table X. Relationship between Subscripts and Internal Coordinates

Subscript	Internal Coordinate
1	Δr_{56}
2	Δr_{15}
3	Δr_{12}
4	Δr_{23}
5	Δr_{34}
6	Δr_{45}
7	$\Delta \alpha_{156}$
8	$\Delta \alpha_{456}$
9	$\Delta \alpha_{154}$
10	$\Delta \alpha_{512}$
11	$\Delta \alpha_{123}$
12	$\Delta \alpha_{234}$
13	$\Delta \alpha_{345}$
14	$\Delta \gamma_{6514}$
15	$\Delta \delta_{5123}$
16	$\Delta \delta_{1234}$
17	$\Delta \delta_{2345}$
18	$\Delta \delta_{3451}$
19	$\Delta \delta_{4512}$

given in Table XI and give a total of $8A_1 + 3A_2 + 5B_1 + 3B_2$ representations. Thus, there are $3A_1 + 2A_2 + B_1 + B_2$ redundancies. The seven redundancies were left in the calculation. Two obvious redundancies are: (a) all ring angles cannot increase and (b) the three angles around the carbon atom cannot increase. The other five redundancies are not obvious.

The symmetry coordinates, S_i, are given in Table XII and were constructed by using the following technique. The sets of symmetrically equivalent internal coordinates were determined by examining the effects of the operations for C_{2v} symmetry upon each internal coordinate. For example, the operations E and $\sigma_v(y,z)$ each transform each internal coordinate into itself (the y and z axes define the plane of the tetrazolate ring with the z axis coincident with the C-H bond, and the x axis is perpendicular to the plane of the ring). For an internal coordinate such as Δr_{15} the operations C_2 and $\sigma_v'(xz)$ each transform Δr_{15} to Δr_{45}, whereas, for Δr_{23} the operations C_2 and $\sigma_v'(xz)$ transform Δr_{23} into itself. Examination of the character for each operation for each irreducible representation determines the proper combination for all equivalent internal coordinates. All symmetry coordinates must be orthogonal and normalized. Thus, the symmetry coordination for the set Δr_{15} and Δr_{45} for the A_1 representation is

$$S_2 = \frac{1}{\sqrt{2}}(\Delta r_{15} + \Delta r_{45}) \qquad (4.19)$$

whereas, for the B_1 representation

$$S_9 = \frac{1}{\sqrt{2}}(\Delta r_{15} - \Delta r_{45}) \qquad (4.20)$$

Table XI. Representations Generated by the Internal Coordinate Sets.

Bond Stretching

Set	Representation
Δr_{56}	A_1
Δr_{12} and Δr_{34}	$A_1 + B_1$
Δr_{23}	A_1
Δr_{15} and Δr_{45}	$A_1 + B_1$

Valence Angle Bending

Set	Representation
$\Delta\alpha_{456}$ and $\Delta\alpha_{156}$	$A_1 + B_1$
$\Delta\alpha_{154}$	A_1
$\Delta\alpha_{512}$ and $\Delta\alpha_{345}$	$A_1 + B_1$
$\Delta\alpha_{123}$ and $\Delta\alpha_{234}$	$A_1 + B_1$

Out of Plane Wagging

Set	Representation
$\Delta\gamma_{6514}$	B_2

Torsional

Set	Representation
$\Delta\delta_{1234}$	A_2
$\Delta\delta_{5123}$ and $\Delta\delta_{2345}$	$A_2 + B_2$
$\Delta\delta_{3451}$ and $\Delta\delta_{4512}$	$A_2 + B_2$

Table XII. Symmetry Coordinates for The Tetrazolate Ion (C_{2v} symmetry).

Species	Symmetry Coordinate	Expression
A_1	S_1	Δr_{56}
	S_2	$\frac{1}{\sqrt{2}}(\Delta r_{15} + \Delta r_{45})$
	S_3	$\frac{1}{\sqrt{2}}(\Delta r_{12} + \Delta r_{34})$
	S_4	Δr_{23}
	S_5	$\frac{1}{\sqrt{2}}(\Delta\alpha_{156} + \Delta\alpha_{456})$
	S_6	$\Delta\alpha_{154}$
	S_7	$\frac{1}{\sqrt{2}}(\Delta\alpha_{512} + \Delta\alpha_{345})$
	S_8	$\frac{1}{\sqrt{2}}(\Delta\alpha_{123} + \Delta\alpha_{234})$
B_1	S_9	$\frac{1}{\sqrt{2}}(\Delta r_{15} - \Delta r_{45})$
	S_{10}	$\frac{1}{\sqrt{2}}(\Delta r_{12} - \Delta r_{34})$
	S_{11}	$\frac{1}{\sqrt{2}}(\Delta\alpha_{156} - \Delta\alpha_{456})$
	S_{12}	$\frac{1}{\sqrt{2}}(\Delta\alpha_{512} - \Delta\alpha_{345})$
	S_{13}	$\frac{1}{\sqrt{2}}(\Delta\alpha_{123} - \Delta\alpha_{234})$

Table XII. (continued).

Species	Symmetry Coordinate	Expression
B_2	S_{14}	$\Delta\gamma_{6514}$
	S_{15}	$\frac{1}{\sqrt{2}}(\Delta\delta_{5123} - \Delta\delta_{2345})$
	S_{16}	$\frac{1}{\sqrt{2}}(\Delta\delta_{3451} - \Delta\delta_{4512})$
A_2	S_{17}	$\frac{1}{\sqrt{2}}(\Delta\delta_{5123} + \Delta\delta_{2345})$
	S_{18}	$\Delta\delta_{1234}$
	S_{19}	$\frac{1}{\sqrt{2}}(\Delta\delta_{3451} + \Delta\delta_{4512})$

The U matrix (see Section II) is obtained from the coefficients of the internal coordinates in the expressions for the symmetry coordinates. The A_1, A_2, B_1, and B_2 species shown in Table XII are Raman active, whereas, the A_1, B_1, and B_2 are infrared active.

The in-plane modes can be separated from the out-of-plane modes. The $5A_1 + 4B_1$ representations are the in-plane vibrational modes, whereas, the $A_2 + 2B_2$ representations are the out-of-plane modes.

The symmetrized force constants, given in Table XIII, were constructed by placing the force constants in tabular (or matrix) form where the internal coordinates label each row and column in an ordered fashion and by using the following rules (30). For a diagonal symmetrized force constant, F_{11}, which corresponds to a particular symmetry coordinate, S_1, the force constant, $f_{1,j}$, in the first row and in the column labeled by a given internal coordinate, ΔR_{ij}, was multiplied by the coefficient, c, with which ΔR_{ij} appeared in the symmetry coordinate, S_1. The product $cf_{1,j}$ was divided by the coefficient, c', of the first internal coordinate (row label). This process was repeated for each column and the results were added. All other diagonal symmetrized force constants were obtained for each symmetry coordinate with the same method. For the off-diagonal force constants, F_{ij}, two different symmetry coordinates must be considered. For each representation the force constant, f_{ij}, in the first row and in the column labeled by a given internal coordinate was multiplied by the coefficient, c, with which that internal coordinate appeared in the symmetry coordinate, S_i. The product cf_{ij} was divided by the

Table XIII. Expressions for the Symmetrized Force Constants.[a]

Species	Symmetrized Force Constant	Expression
A_1	$F_{1,1}$	$f_{1,1}$
	$F_{2,2}$	$f_{2,2} + f_{2,6}$
	$F_{2,3}$	$f_{2,3} + f_{2,5}$
	$F_{2,4}$	$\sqrt{2}\ f_{2,4}$
	$F_{2,5}$	$f_{2,7} + f_{2,8}$
	$F_{2,6}$	$\sqrt{2}\ f_{2,9}$
	$F_{2,7}$	$f_{2,10} + f_{2,13}$
	$F_{2,8}$	$f_{2,11} + f_{2,12}$
	$F_{3,3}$	$f_{3,3} + f_{3,5}$
	$F_{3,4}$	$\sqrt{2}\ f_{3,4}$
	$F_{3,5}$	$f_{3,7} + f_{3,8}$
	$F_{3,6}$	$\sqrt{2}\ f_{3,9}$
	$F_{3,7}$	$f_{3,10} + f_{3,12}$
	$F_{3,8}$	$f_{3,11} + f_{3,12}$
	$F_{4,4}$	$f_{4,4}$
	$F_{4,5}$	$\frac{1}{\sqrt{2}} f_{4,7} + \frac{1}{\sqrt{2}} f_{4,8}$
	$F_{4,6}$	$f_{4,9}$
	$F_{4,7}$	$\frac{1}{\sqrt{2}} f_{4,10} + \frac{1}{\sqrt{2}} f_{4,13}$
	$F_{4,8}$	$\frac{1}{\sqrt{2}} f_{4,11} + \frac{1}{\sqrt{2}} f_{4,12}$
	$F_{5,5}$	$f_{7,7} + f_{7,8}$
	$F_{5,6}$	$\sqrt{2}\ f_{7,9}$

Table XIII. (continued)

Species	Symmetrized Force Constant	Expression
A_1 (cont.)	$F_{5,7}$	$f_{7,10} + f_{7,13}$
	$F_{5,8}$	$f_{7,11} + f_{7,12}$
	$F_{6,6}$	$f_{9,9}$
	$F_{6,7}$	$\frac{1}{\sqrt{2}} f_{9,10} + \frac{1}{\sqrt{2}} f_{9,13}$
	$F_{6,8}$	$\frac{1}{\sqrt{2}} f_{9,11} + \frac{1}{\sqrt{2}} f_{9,12}$
	$F_{7,7}$	$f_{10,10} + f_{10,13}$
	$F_{7,8}$	$f_{10,11} + f_{10,12}$
	$F_{8,8}$	$f_{11,11} + f_{11,12}$
B_1	$F_{9,9}$	$f_{2,2} - f_{2,6}$
	$F_{9,10}$	$f_{2,3} - f_{2,5}$
	$F_{9,11}$	$f_{2,7} - f_{2,8}$
	$F_{9,12}$	$f_{2,10} - f_{2,13}$
	$F_{9,13}$	$f_{2,11} - f_{2,12}$
	$F_{10,10}$	$f_{3,3} - f_{3,5}$
	$F_{10,11}$	$f_{3,7} - f_{3,8}$
	$F_{10,12}$	$f_{3,10} - f_{3,13}$
	$F_{10,13}$	$f_{3,11} - f_{3,12}$
	$F_{11,11}$	$f_{7,7} - f_{7,8}$
	$F_{11,12}$	$f_{7,10} - f_{7,13}$
	$F_{11,13}$	$f_{7,11} - f_{7,12}$

Table XIII. (continued)

Species	Symmetrized Force Constant	Expression
B_1 (cont.)	$F_{12,12}$	$f_{10,10} - f_{10,13}$
	$F_{12,13}$	$f_{10,11} - f_{10,12}$
	$F_{13,13}$	$f_{11,11} - f_{11,12}$
B_2	$F_{14,14}$	$f_{14,14}$
	$F_{14,15}$	$\frac{1}{\sqrt{2}} f_{14,15} - \frac{1}{\sqrt{2}} f_{14,17}$
	$F_{14,16}$	$\frac{1}{\sqrt{2}} f_{14,18} - \frac{1}{\sqrt{2}} f_{14,19}$
	$F_{15,15}$	$f_{15,15} - f_{15,17}$
	$F_{15,16}$	$f_{15,18} - f_{15,19}$
	$F_{16,16}$	$f_{18,18} - f_{18,19}$
A_2	$F_{17,17}$	$f_{15,15} + f_{15,17}$
	$F_{17,18}$	$\sqrt{2}\, f_{15,16}$
	$F_{17,19}$	$f_{15,18} + f_{15,19}$
	$F_{18,18}$	$f_{16,16}$
	$F_{18,19}$	$\frac{1}{\sqrt{2}} f_{16,18} + \frac{1}{\sqrt{2}} f_{16,19}$
	$F_{19,19}$	$f_{18,18} + f_{18,19}$

---

[a] The subscripts for the symmetrized force constants correspond to the subscripts for the symmetry coordinates.

coefficient, c', of the first internal coordinate (row label) which appears in the symmetry coordinate S_j. This was done for each column and the results were added. This process was repeated for all other symmetry coordinate combinations for each particular representation.

V. Results and Discussion

A. Normal Coordinate Analysis Calculation for Sodium Tetrazolate

The normal coordinate analysis calculation was done with the aim of making assignments of the normal modes of vibration (such as bond stretch, ring breathing, etc.) for the tetrazolate anion. Much controversy exists in the literature about the vibrational assignments for tetrazoles. Previous authors have attempted to make vibrational assignments strictly from experimental evidence and by analogy with compounds which contain portions (or subgroups) of the tetrazole ring.

In this calculation the effects of hydrogen bonding due to the water of hydration were neglected. This neglect is a good approximation since all vibrational modes due to hydrogen bonding occur below 200 cm^{-1}. Thus any interactions between those modes and the genuine modes for tetrazole are quite small and would affect the calculated frequencies by only a few cm^{-1}.

The tetrazolate ion vibrations were analyzed by obtaining an initial set of force constants for the internal coordinates and by adjusting these constants so that the observed spectrum was reproduced. The final set of diagonal and interaction constants are listed in Table XIV. Only those interaction constants which caused a significant difference in the calculated frequencies were retained. The interaction force constants, whose difference upon construction of the symmetrized force constants is very small, were neglected. The vibrational frequencies for sodium tetrazolate, calculated by use of the force constants in Table XIV, are given in Table XV. Comparison

Table XIV. Values for Force Constants[a].

$f_{1,1} = 5.268$

$f_{2,2} = 5.36$

$f_{2,3} = 1.05$

$f_{2,4} = 0.50$

$f_{2,5} = 0.35$

$f_{2,6} = 1.45$

$f_{2,7} = -0.12$

$f_{2,8} = -0.009$

$f_{2,9} = 0.13$

$f_{2,10} = 0.13$

$f_{3,3} = 5.21$

$f_{3,4} = 0.57$

$f_{3,5} = 1.05$

$f_{3,10} = 0.30$

$f_{3,11} = 0.35$

$f_{4,4} = 5.56$

$f_{4,5} = 0.57$

$f_{4,6} = 0.50$

$f_{4,11} = 0.25$

$f_{4,12} = 0.25$

$f_{5,5} = 5.21$

$f_{5,6} = 1.05$

$f_{5,12} = 0.35$

$f_{5,13} = 0.30$

$f_{6,6} = 5.36$

$f_{6,7} = -0.09$

$f_{6,8} = -0.12$

$f_{6,9} = 0.13$

$f_{6,13} = 0.13$

$f_{7,7} = 0.58$

$f_{7,8} = 0.28$

$f_{7,9} = -0.22$

$f_{8,8} = 0.58$

$f_{8,9} = -0.22$

$f_{9,9} = 1.44$

$f_{9,10} = 0.28$

$f_{9,11} = 0.15$

$f_{9,12} = 0.15$

$f_{9,13} = 0.28$

$f_{10,10} = 1.34$

$f_{10,11} = 0.28$

$f_{10,12} = 0.15$

$f_{10,13} = 0.40$

$f_{11,11} = 1.39$

$f_{11,12} = 0.50$

$f_{12,12} = 1.39$

$f_{13,13} = 1.34$

$f_{14,14} = 0.297$

$f_{15,15} = 0.201$

$f_{15,16} = -0.006$

$f_{15,19} = -0.006$

$f_{16,16} = 0.201$

$f_{17,17} = 0.201$

$f_{18,18} = 0.201$

$f_{19,19} = 0.201$

---

[a] Units are mdyne/Å .

Table XV. Results of the Normal Coordinate Analysis Calculation for Sodium Tetrazolate.

Species	Vibrational Modes	Calculated[a] Frequency	%E[b]
A_1	ν_1	3125	+0.16%
	ν_2	1461	+0.41%
	ν_3	1243	-3.78%
	ν_4	1138	-1.98%
	ν_5	962	-9.86%
B_1	ν_6	1453	+0.56%
	ν_7	1063	+3.91%
	ν_8	1013	-0.20%
	ν_9	730	+3.99%
B_2	ν_{10}	910	0.00%
	ν_{11}	456	+0.44%
A_2	ν_{12}	537	-----

[a] Units are in cm^{-1}.

[b] $$\%E = \frac{(\nu_{calc.} - \nu_{obs.})}{\nu_{obs.}} 100$$

of the data given in Table XV with the spectral data for sodium tetrazolate monohydrate (Tables XVI and XVII) show that the pattern is reproduced for most frequencies.

From the measured depolarization ratios (Table XVII) for sodium tetrazolate monohydrate the vibrational modes at 3128, 1287, 1189, and 1079 cm^{-1} are symmetric, whereas, the 1438, 1130, 1025, 1009 and 702 cm^{-1} modes are asymmetric. The out-of-plane bands (910, 454 and 537 cm^{-1}) were not observed in the Raman spectrum, which indicates that the polarizability, $\overset{=}{\alpha}$, is quite small for these modes. Thus, the A_2 vibrational mode was not detected. However, since the calculated frequencies for the B_2 modes are in close agreement with the observed frequencies, and since the symmetrized force constants, $F_{17,17}$, $F_{18,18}$ and $F_{19,19}$ (A_2 mode) (Table XIII) differ only in sign from the symmetrized force constants for the B_2 mode which describes the torsional motion, the calculated value is fairly accurate. The observed eigenvalue should not differ from the calculated eigenvalue by more than 5-10 cm^{-1}. The band observed at 1130 cm^{-1} in the Raman, which is observed at 1132 cm^{-1} in the infrared, must be a combination since no calculated asymmetric band has a corresponding energy. Also a band approximately equal to 1130 cm^{-1} is not found for tetrazole (Table IV) or for bis(tetrazolato)copper(II) (Table XIX). Of the five expected A_1 vibrational modes, four are observed in the Raman. The fifth band, ν_2, (ν_2 equals 1455 cm^{-1} in the infrared spectrum) is probably masked by the asymmetric band found at 1437 cm^{-1}. Two other bands, 1696 and 1647 cm^{-1}, are observed in the Raman spectrum. The 1647 cm^{-1} band

Table XVI. Infrared Spectrum for Sodium Tetrazolate Monohydrate with Assignments[a].

Vibrational	Observed Frequency, cm^{-1}	Assignment
	3300	O-H stretch
ν_1	3120	C-H stretch
	2930	$\nu_2 + \nu_6$
	2370	$\nu_2 + \nu_{10}$
	1785	$\nu_5 + \nu_9$
	1685	$\nu_8 + \nu_9$
	1640	O-H bend
ν_2	1455	sym. ring deformation
ν_6	1445	C-H in-plane bend
ν_3	1290	sym. ring deformation
	1210	$\nu_9 + \nu_{12}$(a)
ν_4	1161	sym. ring breathing
	1132	$\nu_9 + \nu_{11}$
ν_5	1065	sym. ring deformation
ν_7	1023	asym. ring deformation
ν_8	1015	asym. ring deformation
ν_{10}	910	C-H out-of-plane bend
ν_9	702	asym. ring deformation
	660	1640-ν_8
ν_{11}	454	out-of-plane ring bend asym. with respect to C_2 axis

[a] ν_{12} is taken as the calculated value.

Table XVII. Raman Spectrum and Depolarization Ratios for Sodium Tetrazolate

Vibrational Mode	Raman Spectrum[a]	Depolarization Ratio[b]
ν_1	3128(m)	0.331
	1696(sh)	-----
	1647(m)	-----
ν_6	1438(s)	0.862
ν_3	1287(vs)	0.432
ν_4	1189(vs)	0.417
	1130(w)	0.858
ν_5	1079(w)	0.242
ν_7	1025(w)	0.897
ν_8	1009(w)	0.875
ν_9	702(w)	0.800

[a] Units are in cm^{-1}.

[b] Intensities were measured with a planimeter.

is due to water, whereas, the 1696 cm^{-1} band is a combination. If a reasonable set of force constants is used, it is impossible to reproduce the observed spectrum within acceptable error so that one of the genuine modes is located at 1696 cm^{-1}. Depolarization ratios could not be measured for the 1647 and 1696 cm^{-1} bands because of fluorescence, which was present from 1500 to 2800 cm^{-1}. Attempts to remove the fluorescing material by passing the aqueous solution of sodium tetrazolate through activated carbon were unsuccessful.

The difference between the calculated frequencies and observed frequencies is quite small except for ν_5 which was calculated to be 962 cm^{-1} versus an observed value of 1065 cm^{-1}. This indicates that the final set of force constants are not completely accurate, however, one can still make the vibrational assignments.

The distribution of each particular vibration among the Cartesian normal coordinates is given in Table XVIII. From the distributions the vibrational assignments were made. Each coefficient was multiplied by the square of the atomic mass, which better describes the relative motion of the atoms with respect to each other. The frequencies, ν_1, ν_6 and ν_{10} (Table XVI) are a C-H stretch, a C-H in-plane bend, and a C-H out-of-plane, respectively. For all other vibrations the ring vibrates as a whole, i.e., there are no particular C-N, N-N, stretching, etc. modes. ν_2, ν_3, and ν_5 are symmetric in-plane-ring deformations, where, ν_4 is a symmetric ring breathing mode. ν_7, ν_8, ν_9 are asymmetric ring deformations. ν_{11} is an out-of-plane ring bend asymmetric with respect to the C_2 axis, whereas, ν_{12} is an out-of-plane ring bend symmetric with respect to the C_2 axis. The

Table XVIII. Distribution of Each Vibration Among the Cartesian Normal Coordinates.

Vibrational Mode	Distribution[a]
1	$-0.094z_5 + 0.941z_6$
2	$-0.061y_1 + 0.111z_1 + 0.082y_2 -0.038z_2 - 0.082y_3 - 0.038z_3 + 0.061y_4 +0.111z_4 - 0.152z_5 - 0.200z_6$
3	$0.127y_1 + 0.024z_1 - 0.058y_2 + 0.053z_2 +0.058y_3 + 0.053z_3 - 0.127y_4 + 0.024z_4 -0.162z_5 - 0.197z_6$
4	$-0.042y_1 + 0.071z_1 - 0.151y_2 -0.078z_2 + 0.151y_3 - 0.078z_3 + 0.042y_4 +0.072z_4 + 0.014z_5$
5	$0.118y_1 + 0.057z_1 + 0.052y_2 - 0.105z_2 -0.052y_3 - 0.105z_3 - 0.118y_4 + 0.057z_4 +0.101z_5$
6	$0.182y_5 - 0.678y_6$
7	$0.058y_1 + 0.099z_1 - 0.127z_2 +0.127z_3 + 0.058y_4 - 0.099z_4 -0.075y_5 - 0.332y_6$
8	$-0.092y_1 + 0.038z_1 + 0.034y_2 - 0.094z_2 +0.034y_3 + 0.094z_3 - 0.092y_4 - 0.038z_4 +0.086y_5 + 0.596y_6$

Table XVIII. (continued)

Vibrational Mode	Distribution[a]
9	$0.058y_1 - 0.106z_1 - 0.103y_3 + 0.078z_3$ $-0.103y_3 + 0.078z_3 + 0.058y_4 + 0.106z_4$ $+0.098y_5$
10	$-0.179x_5 + 0.707x_6$
11	$0.12x_1 - 0.054x_2 - 0.54x_3 + 0.12x_4$ $-0.101x_5 - 0.623x_6$
12	$0.096x_1 - 0.163x_2 + 0.163x_3 - 0.096x_4$

[a] The subscripts refer to the position of the atoms in the ring. The number 6 refers to hydrogen.

remaining bands observed in the infrared spectrum, (Table XVI), are combination bands except the band at 3300 cm^{-1} which is the O-H stretch for water. In all cases for the combinations the direct product of the representation of the two frequencies which form the combination yields a representation which is infrared active and Raman active. The sum of the frequencies which form each combination is in close agreement with the observed frequency. This further substantiates the correct identification of the genuine vibrational modes.

The magnitude of the interaction constants are quite large in most cases. Nakamoto (29) predicts that an interaction constant should have a value of approximately 1/10 the value of the corresponding diagonal force constant. The presence of an unshared pair of electrons on each nitrogen explains the large magnitude. Speculation about the significance of the magnitude of the diagonal force constants is not warranted since the force constants are not of sufficient accuracy. To obtain sufficiently accurate force constants one would have to observe the infrared and/or the Raman spectrum for isotopically substituted sodium tetrazolate.

For the most part the vibrational assignments made by previous authors are not correct. For example, Holm (28) has attributed the band at 664 cm^{-1} to the C-H out-of-plane bend, which would require the force constant, $f_{14,14}$, to be unreasonably low. As it is, $f_{14,14}$ is much smaller than the value calculated ($\sim$0.40 mdyn/Å) for the C-H out-of-plane bend in benzene and the cyclopentadienide ion. Jonassen (19), Holm (28), and LeFebre and Werner (61) have assigned the bands at 1430-60 cm^{-1} to be the N_2N_3 bond. From this investigation all bands in the 1430-60 cm^{-1} region and all other bands, except those associated with C-H, involve complete ring motion rather than just a part of the ring.

B. Synthesis.

Bis(tetrazolato)copper(II) Monohydrate

The pale-blue compound, bis(tetrazolato)copper(II) monohydrate, was prepared by reacting equimolar amounts of aqueous tetrazole and aqueous copper(II) nitrate. The compound decomposes upon heating and is insoluble in all solvents which indicates a polymeric structure.

The reflectance electronic absorption spectrum is given in Table XXI. Fallon (62) has recorded the ultraviolet spectrum of tetrazole. Tetrazole shows no absorption bands below $45.5 \times 10^3 cm^{-1}$. The band at 37.5×10^3 cm^{-1} in the complex probably arises from a transfer of a π electron from the ligand to the $d_{x^2-y^2}$ orbital of the copper atom and not a ligand π to π*electron transfer. A single asymmetric absorption band due to a d-d transition is observed at $14.9 \times 10^3 cm^{-1}$. The copper(II) ion usually exists in octahedral configuration with a tetragonal distortion because of the Jahn-Teller effect, a square planar configuration or a tetrahedral configuration. Of these three possibilities for bis(tetrazolato)copper(II) monohydrate the tetrahedral configuration is not likely because of the magnitude of the Dq value. Ditri *et al.*, (15) observed a splitting of 13.5×10^3 cm^{-1} and 16.0×10^3 cm^{-1} for $Cu(PMT)_6(ClO_4)_2$ and

$Cu(PMT)_4(ClO_4)_2$, respectively. The reflectance spectrum for bis(5-trifluoromethyltetrazolato)copper(II) monohydrate (23) is very similar to that observed for distorted octahedral complexes of copper(II) with strong nitrogen donors (63), and the spectrum is almost identical with the spectra for $Cu(bipy)_3^{2+}$ and $Cu(o\text{-}phen)_3^{2+}$. The principle and most intense band was observed at $14.7 \times 10^3 cm^{-1}$ with a shoulder at $17.9 \times 10^3 cm^{-1}$. A much weaker band was observed at $9.0 \times 10^3 cm^{-1}$. Since the trifluoromethyl group is an electron withdrawing substituent, the tetrazolato ligand should be a stronger ligand than the 5-trifluoromethyltetrazolato ligand, because of the increased electron density on each nitrogen atom. From Ditri's results the energy splitting is larger for the square planar complex than for the six coordinate complex. Thus the coordination of the copper atom in bis(tetrazolato)copper(II) monohydrate complex is probably six-fold with a tetragonal symmetry. The band at $14.7 \times 10^3 cm^{-1}$ is probably the ${}^2B_{1g} \longrightarrow {}^2B_{2g}$ transition. The higher and lower energy transitions, ${}^2B_{1g} \longrightarrow {}^2E_g$ and ${}^2B_{1g} \longrightarrow {}^2A_{1g}$, respectively, could not be resolved. A band was observed at $6.9 \times 10^3 cm^{-1}$ but is probably an overtone of an infrared band ($2 \times 3450 cm^{-1}$) and is not associated with the electronic properties of the complex.

The magnetic moment is given in Table XXII for bis(tetrazolato)-copper(II) monohydrate. The value 1.76 B.M. compares quite closely to the spin-only value of 1.73 B.M. which indicates little spin-orbit coupling. Corrections for the diamagnetism of the ligands and of the

ligands of following compounds were made by use of Pascal's constants (64). Mercury (tetrathiocyanato)cobaltate(II) was used as the standard.

The infrared spectrum for bis(tetrazolato)copper(II) is given in Table XIX. The assignments for the tetrazolate anion were made by analogy from the results for sodium tetrazolate monohydrate. The presence of a band at 544 cm^{-1} substantiates the correctness of the calculated value for the A_2 mode. Ditri and Popov (65) observed two unique bands at 300 cm^{-1} and 276 cm^{-1} for $Cu(PMT)_6(ClO_4)_2$ which they assigned as Cu-N vibrational modes. The two bands at 328 cm^{-1} and 315 cm^{-1} are, by comparison, distinct Cu-N stretches. This observation could indicate two different Cu-N bond distances and would be in accord with the proposed tetragonal symmetry of the complex. Since the copper-nitrogen bond possesses some degree of covalency, the symmetry of the tetrazole ring is at most C_s, and, as a result, only the in-plane and out-of-plane modes are separable. Thus it is not relevant to discuss the ring modes as being symmetrical or asymmetrical. The genuine vibrational modes for the tetrazolate ring are shifted very little as a result of coordination by the copper atom. In all cases the sum of the genuine modes for each combination agrees with the observed band.

Since copper(II) ion is $3d^9$ the electron spin resonance spectrum of bis(tetrazolato)copper(II) would aid in the elucidation of the bonding and structure of the compound. The ESR spectrum for the undiluted powder exhibits a very broad absorption band with a line width of approximately 500 gauss, which indicates that neighboring unpaired electrons interact strongly. The hyperfine splittings were

Table XIX. Infrared Spectrum for Bis(tetrazolato)copper(II) Monohydrate and Vibrational Assignment

Genuine Vibrational Modes	Absorption Maxima	Assignment
ν_{14}	3450 (vs)[a]	O-H stretch
ν_1	3100 (m)	C-H stretch
	2920 (m)	$\nu_2 + \nu_6$
	2350 (w)	$\nu_6 + \nu_{10}$
ν_{13}	1640 (sh)	O-H bend
	1620 (m)	$\nu_5 + \nu_{12}$
ν_2	1470 (s)	ring deformation
ν_6	1450 (s)	C-H in-plane bend
	1390 (m)	$\nu_8 + \nu_{15}$
	1340 (m)	$\nu_7 + \nu_{16}$
ν_3	1240 (m)	ring deformation
	1220 (m)	$\nu_9 + \nu_{12}$
ν_4	1160 (s)	ring breathing
ν_5	1060 (s)	ring deformation
	1045 (sh)	$\nu_9 + \nu_{15}$
ν_7	1020 (s)	ring deformation
ν_8	980 (w)	ring deformation
ν_{10}	900 (vs)	C-H out-of-plane bend
	835 (w)	$\nu_{12} + \nu_{16}$
ν_9	620 (vs)	ring deformation
ν_{12}	544 (s)	out-of-plane ring bend

Table XIX. (continued)

Genuine Vibrational, Modes	Absorption Maxima	Assignment
ν_{11}	450 (m)	out-of-plane ring bend
ν_{15}	328 (s)	Cu-N stretch
ν_{16}	315 (s)	Cu-N stretch

[a] As defined in Table I.

not detected. Attempts to prepare bis(tetrazolato)zinc(II) with copper(II) as an impurity with both water and ethanol as solvents were unsuccessful. Bis(tetrazolato)copper(II) precipitated immediately, whereas, the zinc complex precipitated only after one day.

1-methyl-5-tetrazolyllithium·1/2THF

Since the tetrazolyl anion is isoelectronic with the cyclopentadienyl ion, reactions between various metal ions and the tetrazolyl anion were attempted with the aim of preparing "sandwich-type" compounds. In order to prepare the tetrazolyl anion the reaction between 1-methyl-tetrazole and *n*-butyllithium was attempted. Gilman *et al*., (66) observed that *n*-butyllithium when compared with other *n*-alkyl lithium compounds and phenyllithium is the most reactive. Of the three common solvents (dioxane, ether and tetrahydrofuran) used in organolithium reactions, organolithium compounds are the most reactive in tetrahydrofuran (67).

The white compound, 1-methyl-5-tetrazolyllithium·1/2 tetrahydrofuran was prepared by reacting 1-methyltetrazole with excess *n*-butyllithium in anhydrous tetrahydrofuran at -50°C. The temperature must be kept below -35°C. in order to prevent the lithiumation of the α positions of tetrahydrofuran (68). A reaction time of one-half to one hour was sufficient for complete reaction. 1-methyl-5-tetrazolyllithium·1/2tetrahydrofuran is insoluble in tetrahydrofuran and ether. From the C, H, and N analyses one-half of a mole of tetrahydrofuran is solvated with the lithium compound.

The infrared spectrum for 1-methyl-5-tetrazolyllithium·1/2THF is presented in Table XX. The bands for 1-methyltetrazole at 3135, 1471, and 881 cm^{-1} by analogy with the normal coordinate analysis results for sodium tetrazolate, are the ring C-H stretch, C-H in-plane bend and the C-H out-of-plane bend, respectively. These bands are absent in $LiCH_3N_4$·1/2THF which indicates that the proton at the 5 position was removed. The Li-C stretch for organolithium compounds is found at approximately 880 cm^{-1} (68). Thus the band at 855 cm^{-1} is assigned as the Li-C stretch. No such band is observed for 1-methyltetrazole (Table XX) and bis(1-methyl-5-tetrazolyl)-nickel(II) (Table XXIII). The band at 605 cm^{-1} is very strong and is assigned as the Li-C bend since no such band is observed for 1-methyltetrazole and bis(1-methyl-5-tetrazolyl)nickel(II). The results from the normal coordinate analysis for sodium tetrazolate (Table XVI) were used to determine the ring vibrations for 1-methyltetrazole and 1-methyl-5-tetrazolyllithium·1/2THF. Thus the bands 1496 and 1482, 1279 and 1284, 1174 and 1170, 1113 and 1130, 973 and 970, 928 and 935, and 678 and 673 cm^{-1} should be the in-plane ring vibrations for 1-methyltetrazole and 1-methyl-5-tetrazolyllithium·1/2THF, respectively. The out-of-plane ring modes are 534 and 556, and 476 and 437, respectively. These bands compare favorably with the ring modes assigned for sodium tetrazolate monohydrate. The asymmetric CH_3 and symmetric CH_3 stretches may be assigned as the 2930 and 2880 cm^{-1} bands, respectively, and the asymmetric CH_3 bend and symmetric CH_3 bend may be assigned as 1425 and 1350 cm^{-1} bands, respectively (34).

Table XX. Infrared Spectra of 1-methyl-5-tetrazolyllithium·1/2 THF and 1-methyltetrazole.

Genuine Vibrational Mode	1-methyl-tetrazole	$LiC_2H_3N_4$·1/2THF	Assignment
	3400 (vw), broad	3400 (m), broad	$\nu_7 + \nu_9 + \nu_{17}$
ν_1	3135 (s)		ring C-H stretch
ν_2	2980 (m)	2930 (vs)	asym. CH_3 stretch
ν_3		2880 (sh)	sym. CH_3 stretch
		2830 (w)	$2\nu_7$
		2250 (vw)	$\nu_9 + \nu_{13}$
ν_4		2150 (vs)	C≡N stretch
	1639 (vw)	1610 (w)	$\nu_{11} + \nu_{20}$
ν_5	1496 (s)	1482 (m)	ring vibration
ν_6	1471 (vw)		ring C-H bend
		1460 (s)	due to THF
ν_7	1422 (m)	1425 (s)	asym. CH_3 bend
	1402 (w)	1382 (vw)	$\nu_{14} + \nu_{20}$
ν_8		1350 (s)	sym. CH_3 bend
ν_9	1279 (s)	1284 (vs)	ring vibration
ν_{10}	1225 (m)	1220 (w)	CH_3-N stretch
ν_{11}	1174 (vs)	1170 (w)	ring vibration
		1155 (vw)	$\nu_{18} + \nu_{19}$
ν_{12}	1113 (s)	1130 (w)	ring vibration
	1058 (m)		$2\nu_{19}$
	1040 (w)		$\nu_{17} + \nu_{21}$

Table XX. (continued)

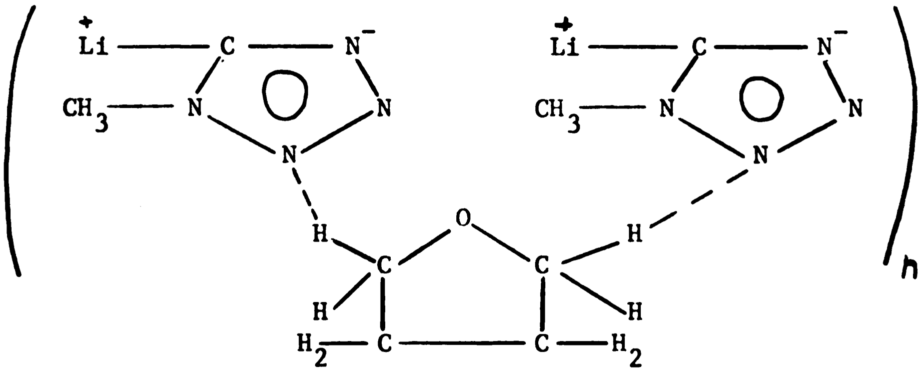
Genuine Vibrational Mode	1-methyl-tetrazole	$LiC_2H_3N_4 \cdot 1/2$ THF	Assignment
ν_{13}	973 (vs)	970 (sh)	ring vibration
ν_{14}	928 (m)	935 (vs)	ring vibration
ν_{15}	881 (vs)		ring C-H out-of-plane wag
ν_{16}		855 (w)	Li-C stretch
	719 (s)		$2\nu_{21}$
ν_{17}	678 (vs)	673 (s)	ring vibration
	658 (s)		$\nu_{13} - \nu_{21}$
ν_{18}		605 (s)	Li-C bend
ν_{19}	534 (s)	556 (m)	out-of-plane ring bend
ν_{20}	476 (s)	437 (m)	out-of-plane ring bend
ν_{21}	357 (m)	354 (sh)	CH_3-N skeletal vibratio

The CH_3-N stretch may be assigned as the 1220 cm^{-1} band and the CH_3-N skeletal vibration as the 354 cm^{-1} band (34). The band at 1460 cm^{-1} is probably the CH_2 deformation for tetrahydrofuran (34). The band at 2150 cm^{-1} is very intense and occurs in the infrared spectrum for bis(1-methyl-5-tetrazolyl)nickel(II) (Table XXIII) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II) (Table XXIV). Because of the intensity this band cannot be a combination. The cyanide stretch for sodium and potassium cyanide occurs at 2080 cm^{-1} while the band for copper(I) cyanide occurs at 2178 cm^{-1}. In copper(I) cyanide the Cu-CN bond is essentially covalent, but in potassium and sodium cyanide the bond is ionic. Since the C≡N stretching band of the free ion is shifted to a higher frequency by coordination, the resonance form (A) is quite important.

$$:C = \ddot{N}\overset{-}{:} \longleftrightarrow :\overset{-}{C}\equiv N:$$

(A) (B)

The band at 2150 cm^{-1} suggests that the delocalization of the electrons is similar in 1-methyl-5-tetrazolyllithium·1/2THF. Thus this compound is probably a polymer with the proposed structure as follows:



This structure would explain the insolubility of the lithium compound in tetrahydrofuran, ether and benzene. The infrared spectrum for the lithium compound, except for the missing C-H bands, is essentially the same as for 1-methyltetrazole which indicates that the tetrazole ring is intact.

Bis(1-methyl-5-tetrazolyl)nickel(II)

Bis(1-methyl-5-tetrazolyl)nickel(II) was prepared by reacting equimolar amounts of 1-methyl-5-tetrazolyllithium and dichlorobis-(triethylphosphine)nickel(II). This compound when wet is extremely sensitive to air and moisture but is much more stable when dry. The compound decomposes when heated and exhibits no detectable solubility in any common solvents which may indicate polymer formation. The nickel complex reacts with the polar, non-donor solvent dinitromethane to form $Ni(C_2H_3N_4)_2 \cdot 2CH_3NO_2$ which decomposes explosively when heated.

The $Ni(C_2H_3N_4)_2$ complex decomposes in ammonia to give CN^-, CH_3OH, and N_3^-.

Methanol and HN_3 were identified by means of vapor phase chromatograms. Methanol was also identified by means of the nmr spectrum. The cyanide ion was identified by the addition of a saturated solution of iron(II) sulfate to an ammonical solution of the complex. To this solution was added aqueous iron(III) chloride. Immediately, a deep blue precipitate formed which indicates the formation of $Fe[Fe(CN)_6]^-$. The close agreement between the calculated and found analysis for cyanide indicates that cyanide ion is formed quantitatively. The compound also dissolves in acidic solutions but not quantitatively.

Only about 55% of the ring decomposes as determined by the analysis for cyanide ion.

From the reflectance spectrum (Table XXI) the symmetry of the nickel ion is octahedral. The bands observed at 8.06×10^3 cm^{-1} and 14.7×10^3 cm^{-1} are the two d-d transitions which correspond to $^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$. The Dq value for $Ni(C_2H_3N_4)_2$ is 806 cm^{-1} which compares with a Dq value of 850 cm^{-1} and 1070 cm^{-1} for $Ni(H_2O)_6^{2+}$ and $Ni(NH_3)_6^{2+}$, respectively (69,70). Thus the 1-methyl-5-tetrazolyl ligand forms a weaker complex than does water. The shoulder at approximately 25.0×10^3 cm^{-1} would be the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transition. From the energy-level diagram for $(3d)^8$ computed by Liehr and Ballhausen (71), the transitions for a regular octahedron should appear at 12.5×10^3 cm^{-1} to 14×10^3 cm^{-1} for $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ and at 23 to 24×10^3 cm^{-1} for $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$. A large charge transfer band was observed at 30.9×10^3 cm^{-1}. Fallon (62) observed no absorption below 43.4×10^3 cm^{-1} for large number 1-alkyltetrazoles. Thus the charge transfer band should be a result of a transfer of a π electron from the tetrazole ring to an e_g orbital of the nickel.

The magnetic moment for bis(1-methyl-5-tetrazolyl)nickel(II) is 2.90 B.M. (Table XXII), and agrees quite well with the spin-only value of 2.83 B.M. The complex has two unpaired electrons and is consistent with the electronic absorption spectrum.

The infrared spectrum is given in Table XXIII. In the main, the features of 1-methyltetrazole are retained but with changes in

Table XXI. The Electronic Absorption Spectra for Some Tetrazole Complexes.

bis(tetrazolato)copper(II) monohydrate	14.9×10^{3} cm^{-1}
	37.5×10^{3} cm^{-1}
bis(1-methyl-5-tetrazolyl)nickel(II)	8.06×10^{3} cm^{-1}
	14.7×10^{3} cm^{-1}
	$\approx 25.0 \times 10^{3}$ cm^{-1} - shoulder
	30.9×10^{3} cm^{-1}
bis(1-cyclohexyl-5-tetrazolyl)nickel(II)	8.33×10^{3} cm^{-1}
	14.7×10^{3} cm^{-1}
	$\approx 26.6 \times 10^{3}$ cm^{-1}
	$\approx 35.1 \times 10^{3}$ cm^{-1}
	$\approx 42.9 \times 10^{3}$ cm^{-1}

Table XXII. The Magnetic Moments for Some Tetrazole Complexes

Compound	Temperature	Magnetic[a] Susceptibility	Experimental Moment, B.M.	Spin-Only Moment	Unpaired Electrons
$Cu(CHN_4)_2 \cdot H_2O$	22.5°C.	1281×10^{-6}	1.76	1.73	1
$Ni(C_2H_6N_4)_2$	24.0°C.	3479×10^{-6}	2.90	2.83	2
$Ni(C_7H_{11}N_4)_2$	22.5°C.	3712×10^{-6}	2.98	2.83	2

[a] Units of χ_M are per mole.

Table XXIII. Infrared Spectrum for Bis(1-methyl-5-tetrazolyl)nickel(II) with Assignments.

Genuine Vibrational Mode	$Ni(C_2H_3N_4)_2$	Assignment
	3400 (m), broad	$\nu_7 + \nu_9 + \nu_{17}$
	3180 (m)	$\nu_5 + \nu_{10} + \nu_{22}$
ν_2	2930(vs)	asym. CH_3 stretch
ν_3	2890 (s)	sym. CH_3 stretch
	2830 (s)	$2\nu_7$
	2250 (vw)	$\nu_9 + \nu_{13}$
ν_4	2150(vs)	C≡N stretch
	1610 (s)	$\nu_{11} + \nu_{20}$
ν_5	1496 (s)	ring vibration
ν_7	1425 (s)	asym. CH_3 bend
ν_8	1348 (vs)	sym. CH_3 bend
ν_9	1284 (vs)	ring vibration
ν_{10}	1223 (w)	CH -N stretch
ν_{11}	1182 (m)	ring vibration
ν_{12}	1125 (w)	ring vibration
	1055 (m)	$2\nu_{19}$
ν_{13}	955 (vs)	ring vibration
ν_{14}	925 (vs)	ring vibration
	755 (w)	$\nu_{20} + \nu_{24}$
ν_{17}	675 (vs)	ring vibration
	660 (s)	$\nu_{13} - \nu_{21}$
ν_{21}	595 (w)	Ni-C bend
ν_{19}	521 (m)	out-of-plane ring vibration

Table XXIII. (continued)

Genuine Vibrational Mode	$Ni(C_2H_3N_4)_2$	Assignment
ν_{22}	456 (w)	Ni-C stretch
ν_{20}	437 (m)	out-of-plane ring bend
ν_{24}	337 (m)	CH_3-N skeletal vibration
ν_{23}	298 (s)	Ni-N stretch

intensities and slight shifts in position of the absorptions. Absorptions occur at 595 and 456 cm^{-1} which are not present for 1-methyltetrazole, and may be attributed to the Ni-C bend and Ni-C stretch, respectively. The Ni-C stretch in $Ni(CN)_4^{2-}$ (72) is found at 543 cm^{-1} and the bend at 433 and 421 cm^{-1}, and the Fe-C stretch (73) in $Fe(CN)_6^{4-}$ is found at 416 cm^{-1} and the bend at 583 cm^{-1}. A band occurs at 298 cm^{-1} which can probably be attributed to an Ni-N bond (65,74) by analogy to nickel PMT and pyridine complexes. The absence of the bands at 3135, 1471, and 881 cm^{-1} confirms the formation of the Ni-C bond. All other vibrational modes were assigned by analogy with 1-methyltetrazole and 1-methyl-5-tetrazolyllithium·1/2THF. The presence of the band at 2150 cm^{-1} indicates considerable electron delocalization around the $-\underset{/}{C}=\underset{\backslash}{N}^{-}$ part of the ring.

Because of the low solubility of the complex in all solvents, the octahedral configuration of Ni and the presence of the Ni-C bonds and Ni-N bonds, the structure is probably polymeric. The tetrazole ring seems to be intact in the complex, if the over-all infrared spectrum is considered and since at least a part of 1-methyltetrazole is recovered, when the complex is decomposed in acid. Since the ring is broken in concentrated ammonia between the 1 and 5 positions and the 3 and 4 positions, it appears that the 1-5 N-C and the 3-4 N-N bonds may be rather ionic.

Because nickel is six coordinate, each ligand must provide three bonds. Two of the six bonds to each nickel are Ni-C bonds, while, the other four are Ni-N bonds. If the resonance form $-\underset{/}{C}=\underset{\backslash}{N}{:}^{\ominus}$ is apropos, the bond between the 4 nitrogen and Ni would be essentially ionic. The remaining two bonds are probably covalent bonds formed between the 2 or 3 nitrogen of an adjacent ring and the nickel of the original unit. By working with Framework Molecular Models it was not possible to form a unit where the Ni-C bond is from one ring, the Ni-N_4 bond from another ring and the Ni-$N_{2 \text{ or } 3}$ bond from a third ring. Also, it is not possible sterically to form a unit where the Ni-C and Ni-$N_{2 \text{ or } 3}$ bonds are formed from the same ring and the Ni-N_4 from a second ring. If the Ni-N_4 bond is covalent rather than ionic, the Ni-C and Ni-N_4 bonds possess considerable strain because of the formation of a three membered ring. If the Ni-C and each set of Ni-N bonds are cis, the simplest unit formed is a hexamer. This is not likely since the hexamer should be soluble in non-polar solvents. If the Ni-C and each set of Ni-N bonds are trans, an infinite array is formed, which is compatible with the insolubilities of the complex.

Crystal structures have been determined for pentamethylene iodine monochloride and dichlorobis(1-methyltetrazole)zinc(II (75,76). In both cases coordination involved the 4 position of the tetrazole ring. Even though PMT-ICl and $Zn(C_2H_4N_4)Cl_2$ are not analogous with $Ni(C_2H_3N_4)_2$ the crystal-structural results tend to indicate that the 4 position of the tetrazole ring is unique and, thus, probably is involved in the coordination of $Ni(C_2H_3N_4)_2$.

Bis(1-cyclohexyl-5-tetrazolyl)nickel(II)

The reaction between 1-cyclohexyl-5-tetrazolyllithium (prepared *in situ*) and dichlorobis(triethylphosphine)nickel(II) yielded pale-green bis(1-cyclohexyl-5-tetrazolyl)nickel(II) after a period of one to two days. The compound decomposes with heating, is insoluble in all solvents and is sensitive to the atmosphere.

The compound decomposes in ammonia to give CN^-, N_3^- and cyclohexyl alcohol similar to what was observed for bis(1-methyl-5-tetrazolyl)-nickel(II).

The reflectance spectrum (Table XXI) shows two distinct bands at 8.33×10^3 cm^{-1} and 14.7×10^3 cm^{-1}, d-d transitions, which correspond to $^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$, respectively. The Dq value for the compound is 833 cm^{-1}. The data indicate that the 1-cyclohexyl-5-tetrazolyl ligand forms a slightly stronger complex than does the 1-methyl-5-tetrazolyl anion. A broad band was observed at approximately 26.6×10^3 cm^{-1} which is the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transition. If the transitions $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ were observed at 14 to 15×10^3 cm^{-1} and 24 to 25×10^3 cm^{-1} the symmetry would correspond to that of a regular octahedron. Two broad charge transfer bands were observed at approximately 35.1×10^3 cm^{-1} and 42.9×10^3 cm^{-1} which are probably due to a ligand π electron transfer to the e_g orbital and a ligand π to π^* transfer, respectively.

The magnetic moment (Table XXII) is 2.98 B.M. versus a spin-only value of 2.83 B.M. The presence of two unpaired electrons is in agreement with the reflectance spectra.

The infrared spectrum, presented in Table XXIV, shows several interesting features. The Ni-C bend was observed at 581 cm^{-1}. This absorption is slightly lower than that observed for $Ni(C_2H_3N_4)_2$,

Table XXIV. Infrared Spectra for Bis(1-cyclohexyl-5-tetrazolyl)-nickel(II) and 1-cyclohexyltetrazole.

Genuine Vibrational Mode	1-cyclohexyl-tetrazole	$Ni(C_7H_{11}N_4)_2$	Assignment[a]
		3420 (s)	1370 + 1350 + ν_7
ν_1	3125 (s)		ring C-H stretch
	2930 (vs)	2930 (vs)	R[b] C-H stretch
	2850 (s)	2850 (s)	R C-H stretch
	2650 (w)	2650 (w)	1338 + 1302
		2520 (w)	1370 + 1146
		2130 (vs)	C≡N stretch
	1740 (vw)	1710 (s)	$\nu_3 + \nu_9$
	1610 (vw)	1622 (s)	$\nu_3 + \nu_{10}$
ν_2	1470 (s)		ring C-H bend
	1450 (vs)	1450 (vs)	*
	1424 (m)		ν_4 + 337
	1404 (w)		1054 + 337
	1366 (m)	1370 (m)	*
		1350 (m)	900 + ν_{10}
	1344 (w)	1338 (w)	*
	1310 (m)	1302 (m)	*
	1266 (m)	1262 (s)	*
	1242 (w)	1241 (w)	*
		1215 (s)	900 + ν_{11}
ν_3	1180 (sh)	1185 (w)	ring vibration

Table XXIV. (continued)

Genuine Vibrational Mode	1-cyclohexyl-tetrazole	$Ni(C_7H_{11}N_4)_2$	Assignment
	1167 (vs)	1163 (w)	*
	1138 (s)	1146 (w)	*
ν_4	1101 (vs)	1095 (w)	ring vibration
		1078 (w)	ν_9 + 466
	1054 (m)	1044 (vw)	*
	1032 (m)	1031 (m)	*
ν_5	1001 (s)	1000 (vw)	ring vibration
	970 (s)	955 (vs)	*
	920 (vw)	900 (vs)	*
	897 (vs)	895 (vs)	*
ν_6	881 (vs)		ring C-H out-of-plane bend
		858 (s)	ν_9 + 337
	820 (s)	802 (sh)	*
		790 (s)	466 + ν_{11}
	746 (s)		$\nu_3 - \nu_{10}$
	718 (vw)		1266 - ν_{10}
ν_7	675 (vs)	695 (s)	ring vibration
	659 (vs)		2(337)
ν_8		581 (m)	Ni-C bend
ν_9	554 (m)	523 (m)	out-of-plane-ring vibration
	468 (m)	466 (m)	*

Table XXIV. (continued)

Genuine Vibrational Mode	1-cyclohexyl-tetrazole	$Ni(C_7H_{11}N_4)_2$	Assignment[a]
ν_{10}	439 (s)	444 (m)	out-of-plane-ring vibration
		366 (m)	1262 - 900
	337 (m)	337 (m)	*
ν_{11}		316 (sh)	Ni-N stretch
	242 (m)		1344 - 1101 or 1138 - 897

[a] * implies a vibration due to the cyclohexyl group.

[b] R indicates cyclohexyl.

which indicates that the Ni-C bond is slightly weaker. No frequency which could be attributed to the Ni-C stretch was observed. The Ni-C stretch is probably masked by the 466 and/or 444 cm^{-1} bands. A shoulder was observed at 316 cm^{-1} which has been attributed to the Ni-N bond and this band is absent in the 1-cyclohexyltetrazole infrared spectrum. The band at 2130 cm^{-1}, CN bond, indicates that the bonding in $Ni(C_7H_{11}N_4)_2$ is approximately the same as in $Ni(C_2H_3N_4)_2$. The proton has been removed from the 5 position in the complex because the absorption bands due to the C-H ring vibrations are missing. The vibrational modes due to the cyclohexyl substituent were determined by comparing the infrared spectrum of 1-cyclohexyltetrazole with those for cyclohexanol and cyclohexyl amine. Not all of the ring vibrational modes were observed because of masking by the cyclohexyl modes.

In general the results for bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II) are the same. Thus the bonding characteristics should be identical.

References

1. Benson, F. R., Chem. Rev., 41, 1(1947).

2. Benson, F. R., "Heterocyclic Compounds", 39, Interscience Publishers, New York, 1967.

3. Popov, A. I., Bisi, C. C., and Craft, M., J. Am. Chem. Soc., 80, 6513(1958).

4. Popov, A. I., Wehman, T. C., and Vaughn, J. W., J. Inorg. Nuclear Chem., 26, 2027(1964).

5. Person, W. B., Humphrey, R. E., Deskin, W. A., and Popov, A. I., J. Am. Chem. Soc., 80, 2049(1958).

6. Bladin, J., Ber., 25, 1413(1892).

7. Olivera-Mandala, E., and Alagna, B., Gazz. Chim. Ital., 40, II, 441(1910).

8. Herbst, R. M., and Garbrecht, W. L., J. Org. Chem., 18, 1283 (1953).

9. Herbst, R. M., and Mihina, J. S., J. Org. Chem., 15, 1082 (1950).

10. Rheinboldt, H., and Stelliner, H., Bol. fac. filosof. cien., Univ. Sao Paulo, Quimica 1, 27(1942); C.A. 40, 1502(1943).

11. Dister, A., J. Pharm. Belg., 3, 190(1948).

12. Zwikker, J. J. L., Pharm.Weekblad, 71, 170(1934).

13. Popov, A. I., and Holm, R. D., J. Am. Chem. Soc., 81, 3250(1959).

14. D'Itri, F. M., and Popov, A. I., Inorg. Chem., 6, 597(1967).

15. D'Itri, F. M., and Popov, A. I., ibid., 5, 1670(1966).

16. Brubaker, C. H., Jr., J. Am. Chem. Soc., 82, 82(1960).

17. Daugherty, N. A., and Brubaker, C. H., Jr., ibid., 83, 3779(1961).

18. Daugherty, N. A., and Brubaker, C. H., Jr., J. Inorg. Nuclear Chem., 22, 193(1961).

19. Harris, A. D., Herber, R. H., Jonassen, H. B., and Wertheim, G. K., J. Am. Chem. Soc., 85, 2927(1963).

20. Jonassen, H. B., Terry, J. O., and Harris, A. D., J. Inorg. Nuclear Chem., 25, 1239(1963).

21. Gilbert, G. L., and Brubaker, C. H., Jr., Inorg. Chem., 2, 1216(1963).

22. Kuska, H. A., D'Itri, F. M. and Popov, A. I., ibid., 5, 1272(1966).

23. Harris, A. D., Jonassen, H. B., and Archer, R. D., ibid., 4, 147(1965).

24. Jonassen, H. B., and Smith, R., private communication.

25. Stolle, R., Ehrmann, K., Reider, D., Wille, H., Winter, H., and Henke-Stark, F., J. Prakt. Chem., 134, 282(1932).

26. Gilbert, G. L., Ph.D. Thesis, Michigan State University, East Lansing, Michigan(1963).

27. Beck, W., and Fehlhammer, W. P., Angew. Chem., 79, 146(1967).

28. Holm, R. D., and Donnelly, P. L., J. Inorg. Nuclear Chem., 28, 1887(1966).

29. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, New York, 1963.

30. Wilson, E. B., Jr., Decius, J. C. and Cross, P. C., "Molecular Vibrations", McGraw-Hill Book Co., New York, 1955.

31. Tobias, R. S., J. Chem. Educ., 44, 2(1967).

32. Tobias, R. S., ibid., 44, 70(1967).

33. Herzberg, Gerhard, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, Inc., New York, 1945.

34. Bellamy, L. J., "The Infra-red Spectra of Complex Molecules", John Wiley and Sons, Inc., 1954.

35. Sutherland, G. B. B. M., "Infrared and Raman Spectra", Methuen, London, 1935.

36. Kohlrausch, K. W. F., "Ramanspektrem", Vol. 9, Sec. VI of Eucken-Wolf, "Hand- und Jahrbuch der Chemischen Physik", Akadomische Verlagsgesellschaft, Leipzig, 1943. Reprinted by Edwards, Ann Arbor, Mich., 1945.

37. Barrow, Gordon M., "Introduction to Molecular Spectroscopy", McGraw-Hill Book Co., New York, 1962.

38. Cotton, F. A., "Chemical Applications of Group Theory", Interscience Publishers, John Wiley and Sons, Inc., New York, 1963.

39. Mizushima, S. and Shimanouchi, T., "Infrared Absorption and the Raman Effect", Kyoritsu, Tokyo, 1958.

40. Meisler, A. G., and Cleveland, F. F., "Molecular Spectra II", Publs. Ill. Inst. Technol., 1948.

41. Wilson, E. B., Jr., J. Chem. Phys., 7, 1047(1939).

42. Wilson, E. B., Jr., ibid., 9, 76(1941).

43. Garbrecht, William L., Ph.D. Thesis, Michigan State University, East Lansing, Michigan.

44. Ugi, I., Meyr, R., Lipinski, M., Bodesheim, F., and Rosendahl, F., Org. Syn., 41 13(1961).

45. Ugi, I., and Meyr, R., Ber., 93, 239(1960).

46. Fallon, Frances G., and Herbst, M., J. Org. Chem., 22, 933(1957).

47. Pray, A. R., "Inorganic Synthesis", 5, 153, McGraw-Hill Book Co., Inc., New York, 1957.

48. Kovacic, P., and Brace, N. O., ibid., 6, 172, McGraw-Hill Book Co., Inc., New York, 1960.

49. Jensen, K. A., Nielson, Per F., Pederson, C. Th., Acta Chem. Scand., 17, 1115(1963).

50. Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis", The MacMillan Co., New York, 1943, pp. 574 ff.

51. Schachtschneider, J. H., "Vibrational Analysis of Polyatomic Molecules. III. Vibrational Secular Equation Programs", Technical Report No. 263-2, Shell Development Co., Emeryville, California.

52. Synder, R. G. and Schachtschneider, J. H., Spectrochim. Acta, 19, 117(1963).

53. Bodegig, E., "Matrix Calculus", 2nd ed., North-Holland Publishing Co., Amsterdam, 1959, pp. 329 ff.

54. Palenik, Gus J., Acta Cryst., 16, 596(1963).

55. Badger, R. M., J. Chem. Phys., 2, 128(1933).

56. Badger, R. M., ibid., 3, 710(1934).

57. Ibid., Phys. Rev., 48, 284(1935).

58. Herschbach, D. R., and Laurie, V. W., J. Chem. Phys., 35, 458(1961).

59. Lippincott, E. R., and Nelson, R. D., Spectrochim. Acta, 10, 307(1958).

60. Kakiuti, Y., and Shimarouchi, T., J. Chem. Phys., 25, 1252(1956).

61. LeFebre, R. J. W. and Werner, R. L., Australian J. Chem., 10, 26(1957).

62. Fallon, F. G., Ph.D. Thesis, Michigan State University, East Lansing, Michigan, 1956.

63. Manch, W. and Fernelius, W. C., J. Chem. Ed., 38, 192(1961).

64. Figgis, B. N. and Lewis, J., "Modern Coordination Chemistry", Interscience Publishers Inc., New York, 1960, p. 403.

65. D'Itri, F. M. and Popov, A. I., Inorg. Chem., in press.

66. Gilman, H., and Kirby, R. H., J. Am. Chem. Soc., 55, 1265(1933).

67. Gilman, H., and Gray, S., J. Org. Chem., 23, 1476(1958).

68. Coates, G. E., "Organo-Metallic Compounds", John Wiley and Sons, Inc., New York, 1960, pp. 1 ff.

69. Jorgensen, C. K., Acta Chem. Scand., 9, 1362(1955).

70. Ibid., 10, 887(1956).

71. Liehr, A. D., and Ballhausen, C. J., Ann Phys., (N. Y.) 6, 134(1959).

72. McCullough, R. L., Jones, L. H., and Crosby, G. A., Spectrochim. Acta, 16, 929(1960).

73. Jones, L. H., Inorg. Chem., 2, 777(1963).

74. Frank, C. W., and Rodgers, L. B., ibid., 5, 615(1966).

75. Bloor, J., Tulinsky, A., and Popov, A. I., private communication.

76. Baenziger, N. C., private communication.