A Vibrational Analysis of the Tetrazolate Ion and the Preparation of Bis(tetrazolato)copper(II)

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Abstract: 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_1 modes and the 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 (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, corroborated by the measurement of the depolarization ratios, are 3120, 1290, 1161, and 1065 cm^{-1}. The fifth A_1 mode, 1455 cm^{-1} in the infrared, 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. The pale blue complex, bis(tetrazolato)copper(II) monohydrate, is insoluble in all common solvents and appears from the reflectance spectrum to be six-coordinate. The insolubility indicates a polymeric structure. Two bands at 328 and 315 cm^{-1} are attributed to Cu–N bonds. Other infrared absorptions can be associated with the tetrazolate ion. The magnetic moment of 1.76 BM indicates one unpaired electron.

Recently Holm and Donnelly[1] have prepared tetrazolate complexes of iron(II), nickel(II), cobalt(II), zinc(II), and cadmium(II). No other investigations have concerned complexation by unsubstituted tetrazole.

The N–H normal vibrational modes for some 5-aminotetrazole compounds have been identified by Jonassen, *et al.*[2] The vibrational modes which may be attributed to the tetrazole ring have been tentatively assigned by comparing the infrared spectra of a large number of substituted tetrazoles.[1-6]

Since no theoretical analysis of the vibrational spectrum of any tetrazole has been reported, we have performed a vibrational analysis of the tetrazolate ion. The structure and numbering of the tetrazolate ion is
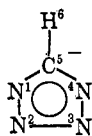
Experimental Section

Materials. Reagent grade chemicals were used throughout this investigation. Tetrazole was prepared by the diazotiation of 5-aminotetrazolate.[7] Sodium tetrazolate monohydrate was prepared by method of Holm, *et al.*[1] Purity was confirmed by comparing melting points and infrared spectra with previously reported values.[1,7]

Preparation of Bis(tetrazolato)copper(II) Monohydrate. To 0.02 mole of tetrazole in 50 ml of water was added dropwise 0.0095

mole of copper(II) nitrate trihydrate in 50 ml of water, and the solution was stirred continuously. Immediately a pale blue solid precipitated. The solution was stirred for 4 hr, filtered, and washed repeatedly with water, ethyl acetate, ethanol, and ether to remove any remaining reactants. A yield of 82% based on the amount of copper nitrate trihydrate was obtained.

Anal. Calcd for Cu(CHN₄)₂·H₂O: 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.

Analytical Methods. The percentage of copper was determined spectrophotometrically as in earlier studies.[5] Analyses for carbon, hydrogen, and nitrogen were made by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Reflectance Spectrum. The reflectance spectrum was measured with a Beckman Model DK2 spectrometer with diffuse reflectance attachment and a Cary Model 15 spectrophotometer 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 in. × 2 in. aluminum plate with a cylindrical bore (1 in. × 1/16 in.) was used as a sample holder with the Beckman DK2. All samples were prepared with two parts of magnesium oxide or silica to one part of sample. The samples were tamped into the holder so that none would fall into the reflectance cavity.

Magnetic Susceptibility Measurement. The Gouy method was used to obtain the magnetic moments at room temperature. Hg[Co(SCN)₄] was used as a standard. The moments were corrected for the diamagnetism of the ligands by use of Pascal's constants.[8]

Infrared Spectra. Infrared spectra of the compounds were recorded on a Unicam SP-200 spectrophotometer with potassium bromide disks or with Nujol or 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.

Raman Spectra. The unpolarized and polarized Raman spectra for 1 and 3 M aqueous solutions of sodium tetrazolate monohydrate were obtained by use of 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 was used

(1) R. D. Holm and P. L. Donnelly, *J. Inorg. Nucl. Chem.*, **28**, 1887 (1966).
(2) H. B. Jonassen, T. Paukert, and R. A. Henry, *Appl. Spectry.*, **21**, 89 (1967).
(3) E. Lieber, D. Levering, and L. Patteman, *Anal. Chem.*, **23**, 1594 (1951).
(4) C. N. R. Rao and R. Ventkataveghaven, *Can. J. Chem.*, **42**, 43 (1964).
(5) C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, **82**, 82 (1960).
(6) A. D. Harris, R. H. Herber, H. B. Jonassen, and G. K. Wertheim, *ibid.*, **85**, 2927 (1963).
(7) R. A. Henry and W. G. Finnegan, *ibid.*, **76**, 290 (1954).

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

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}/mm on a photographic plate. The resolution was 10-15 cm^{-1}. The spectra were recorded on Eastman Kodak II a-o spectroscopic plates preheated under vacuum for 12 hr.

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

Results and Discussion

The pale blue compound bis(tetrazolato)copper(II) monohydrate was prepared by the reaction of a slight excess of aqueous tetrazole with aqueous copper(II) nitrate. The compound decomposes upon heating and is not soluble in any common solvent. The insolubility probably indicates a polymeric structure.

The reflectance spectrum exhibits an asymmetric band at 14.9 $\times$ 10^3 and a broad band at 37.5 $\times$ 10^3 cm^{-1}. Fallon[9] 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 $\times$ 10^3 cm^{-1} in the complex probably arises from a transfer of a π electron from the ligand to the $d_{z^2-y^2}$ orbital of copper and not a ligand π to π^* electron transfer. D'Itri and Popov[10] observed absorptions at 13.5 and 16.0 $\times$ 10^3 cm^{-1} for Cu(PMT)$_6$(ClO$_4$)$_2$ and Cu(PMT)$_4$(ClO$_4$)$_2$, respectively, where PMT is pentamethylenetetrazole. The reflectance spectrum for bis(5-trifluoromethyl-tetrazolato)copper(II) monohydrate[11] is very similar to that observed for distorted octahedral complexes of copper(II) with strong nitrogen donors,[12] and the spectrum is almost identical with that of Cu(bipy)$_3{}^{2+}$. The principal 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}. Since the trifluoromethyl group is an electron-withdrawing substituent, the tetrazolato ligand should be a stronger ligand than the 5-trifluoromethyltetrazolato ligand. Thus the coordination of the copper atom in the complex is probably sixfold with a tetragonal symmetry. The band at 14.7 $\times$ 10^3 cm^{-1} is probably the $^2B_{1g} \rightarrow$ $^2B_{2g}$ transition. The higher and lower energy transitions, $^2B_{1g} \rightarrow$ ^2E_g and $^2B_{1g} \rightarrow$ $^2A_{1g}$, respectively, could not be resolved.

The magnetic moment is 1.76 BM and compares quite closely to the spin-only value of 1.73 BM which indicates little spin-orbit coupling.

The infrared spectrum for bis(tetrazolato)copper(II) monohydrate is given in Table I. The assignments for the tetrazolate anion were made by analogy from the results for sodium tetrazolate (see following discussion). D'Itri and Popov[13] observed two unique bands at 300 and 276 cm^{-1} for Cu(PMT)$_6$(ClO$_4$)$_2$ which they assigned as Cu-N vibrational modes. The two bands at 328 and 315 cm^{-1} are due to two distinct Cu-N bonds 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 rele-

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

Genuine vibrational modes	Absorption maxima[a]	Assignment
ν_{14}	3450 (vs)	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)	$\nu_5 + \nu_{15}$
	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_{19}	690 (vs)	Ring deformation
ν_{12}	544 (s)	Out-of-plane ring bend
ν_{11}	450 (m)	Out-of-plane ring bend
ν_{15}	328 (s)	Cu-N stretch
ν_{16}	315 (s)	Cu-N stretch

[a] vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder.

vant 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. Some bands are observed which are believed to be combinations and the sums of genuine modes for each combination agree with the observed band.

Since copper(II) ion is 3d^9, the electron spin resonance spectrum of the complex would aid in the elucidation of the bonding and structure of the compound. Kuska, et al.,[14] observed the copper hyperfine splittings in the undiluted samples of Cu(PMT)$_6$(ClO$_4$)$_2$ and Cu(PMT)$_4$(ClO$_4$)$_2$; however, we observed (for the undiluted powder) a very broad absorption band with a line width of approximately 500 G. Attempts to prepare bis(tetrazolato)zinc(II) with copper(II) as an impurity with both water and ethanol as solvents were unsuccessful. The copper complex precipitated immediately, while the zinc complex precipitated only after 1 day.

The Wilson FG matrix technique[15] has been used for a normal coordinate ayalysis of the tetrazolate ion. A general FORTRAN program described by Snyder and Schachtschneider,[16] as modified by Sachse[17] to include the FORTRAN coordinate routine described by Schwendeman,[18] was used to perform the calculation. All calculations were carried out on the Michigan State University Control Data 3600 digital computer.

The G matrix was evaluated in the usual manner[15] from the structural parameters for sodium tetrazolate

(9) F. G. Fallon, Ph.D. Dissertation, Michigan State University, East Lansing, Mich., 1956.

(10) F. M. D'Itri and A. I. Popov, Inorg. Chem., 5, 1670 (1966).

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

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(13) F. M. D'Itri and A. I. Popov, Inorg. Chem., 6, 1591 (1967).

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

(15) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

(16) R. G. Snyder and J. H. Schachtschneider, Spectrochim. Acta, 19, 117 (1963).

(17) H. P. E. Sachse, private communication.

(18) R. H. Schwendeman, J. Mol. Spectry., 6, 301 (1961).

monohydrate[19] listed in Table II in terms of a set of internal displacement coordinates. For the calculation, 19 internal coordinates, R, were selected as follows: 13 in-plane coordinates, which include six bond stretching (r) and seven valence angle bending (α), and six out-of-plane coordinates, which include a C–H out-of-plane wagging coordinate (γ) and five torsional motions about the ring (δ).

Table II. Structural Parameters of Sodium Tetrazolate

$$r_{12} = r_{34} = 1.348 \text{ A}$$
$$r_{23} = 1.310 \text{ Å}$$
$$r_{15} = r_{45} = 1.329 \text{ Å}$$
$$r_{56} = 0.911 \text{ Å}$$
$$\angle 456 = \angle 156 = 123.8°$$
$$\angle 154 = 112.4°$$
$$\angle 512 = \angle 345 = 104.3°$$
$$\angle 123 = \angle 234 = 109.5°$$

^{a} The subscripts refer to the position of the atoms in the ring. Number 6 refers to hydrogen.

The following notation will be used for the internal coordinates: r_{ij} = stretching of bond which connects atoms i and j; α_{ijk} = bending of valence angle between bonds ij and jk; γ_{ijkl} = out-of-plane wagging of bond ij connected to the bonds jk and jl; δ_{ijkl} = change of torsional angle between bonds ij and kl about the bond which connects atoms j and k. i, j, k, and l are atoms of the ring.

It is convenient to employ G and F matrices expressed in terms of a set of symmetry coordinates S appropriate for the C_{2v} point group of the tetrazolate ion, as shown in Table III. The relationships to the corresponding quantities in terms of the internal coordinates R are given by

$$S = UR$$
$$\mathrm{G} = UG\tilde{U}$$
$$\mathrm{F} = UF\tilde{U} \qquad (1)$$

where U is an orthogonal transformation matrix,[15] G is the symmetrized kinetic energy matrix, and F is the symmetrized potential energy matrix.

The genuine vibrations of the tetrazolate ion reduce to the representations $5 A_1 + A_2 + 4B_1 + 2 B_2$, so that $3 A_1 + 2 A_2 + B_1 + B_2 = 7$ redundancies are included. The redundant coordinates were retained in the calculation, but the diagonalization was carried out so that a zero frequency resulted for each redundancy and only 12 genuine frequencies resulted.

A modified valence force field (mvff) was assumed for F. Initial estimates for the mvff potential constants were made in the following manner: the C–H stretching frequencies was separated in species A_1, and all interaction constants between C–H stretching and other internal coordinates were taken as zero; stretching force constants were calculated from the Herschbach–Laurie modification[20] of Badger's rule[21] from the structural parameters given in Table II; in-plane angle bending constants were transferred from the cyclopentadienide ion;[22] and potential constants for out-of-plane motions

(19) G. J. Palenik, *Acta Cryst.*, **16**, 596 (1963).
(20) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **35**, 458 (1961).
(21) R. M. Badger, *ibid.*, **3**, 710 (1934).

Table III. Symmetry Coordinates for the Tetrazolate Ion (C_{2v} Symmetry)

Species	Symmetry coordinate	Symmetry coordinate expression
A_1	S_1	$\Delta r_{56}{}^a$
	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}	$\frac{1}{\sqrt{2}}(\Delta \alpha_{123} - \Delta \alpha_{234})$
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}	$\frac{1}{\sqrt{2}}(\Delta \delta_{3451} + \Delta \delta_{4512})$

^{a} The subscripts refer to the positions of the atoms in the ring. Number 6 refers to hydrogen.

were taken from benzene.[23] An initial symmetrized F matrix was then calculated by eq 1 for use in the calculation.

The symmetrized potential constants were adjusted so that a reasonable fit was obtained between calculated and observed eigenvalues, and so that the force constants in the internal coordinate representation had reasonable values. During the adjustment, interaction constants in the symmetrized F matrix were added successively and varied over a range of values, negative and positive. Those which were found to be small and which had only a small effect on the calculated eigenvalues were neglected.

The comparison between observed and calculated eigenvalues is shown in Table IV. The mvff constants for the internal coordinate representation may be calculated from the symmetrized force constants by eq 1, and the results are given in Table V.

The assignment of the fundamental frequencies was corroborated by determining the depolarization ratios for the Raman spectrum of a solution of sodium tetrazolate. The results shown in Table VI indicate clearly

(22) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).
(23) Y. Katiuti and T. Simarouchi, *J. Chem. Phys.*, **25**, 1252 (1956).

Table IV. Observed $(\nu)^a$ and Calculated Fundamentals
(ν') with Assignments for Sodium Tetrazolate Monohydrate

Species	No.	Description	ν^b	ν'^b
A₁	1	C–H stretch	3120 (sh)^d	3124
	2	Sym ring deformation	1445 (s)	1461
	3	Sym ring deformation	1290 (s)	1243
	4	Sym ring breathing	1161 (vs)	1138
	5	Sym ring deformation	1065 (vs)	962
B₁	6	C–H in-plane bend	1445 (s)	1453
	7	Asym ring deformation	1023 (vs)	1063
	8	Asym ring deformation	1015 (vs)	1013
	9	Asym ring deformation	702 (vs)	730
B₂	10	Out-of-plane C–H wag	910 (vs)	910
	11	Out-of-plane ring bend Symmetric with respect to C₂ axis	454 (w)	456
A₂	12	Out-of-plane ring bend asymmetric with respect to the C₂ axis		537
H₂O		O–H stretch	3300 (vs)	
H₂O		H–O–H bend	1640 (sh)	
		$\nu_2 + \nu_6$	2930 (m)	2900^c
		$\nu_2 + \nu_{10}$	2370 (m)	2365
		$\nu_5 + \nu_9$	1785 (m)	1767
		$\nu_8 + \nu_9$	1785 (s)	1717
		$\nu_9 + \nu_{12}$	1210 (s)	1239
		$\nu_9 + \nu_{11}$	1132 (m)	1156
		$1640 - \nu_8$	660 (w)	625

^{a} The observed values were taken from the infrared spectrum. ^{b} Units are in cm⁻¹. ^{c} Combination bands calculated from observed fundamentals except ν_{12}. ^{d} As defined in Table I.

cm⁻¹ (species B₂) were not observed in the Raman spectrum and were assigned from the infrared spectrum. The A₂ band at 537 cm⁻¹ which is Raman active only was not observed and was assigned from the calculated results. The symmetrized force constants for the A₂ species differ only in sign from those of the B₂ torsional mode, which is in close agreement with the observed frequency, and thus the calculated value for the A₂ species should be fairly accurate. The assignment is consistent with an observed band at 1210 cm⁻¹ which we interpret as a combination $\nu_9 + \nu_{12} = 1239$ cm⁻¹ (calculated). The calculated value for the A₂ mode should be accurate to within 5–10 cm⁻¹.

The asymmetric band observed at 1130 cm⁻¹ in the Raman and at 1132 cm⁻¹ in the infrared must be a combination since there is no calculated asymmetric frequency in this region. Moreover, the infrared spectra of tetrazole[1] and of bis(tetrazolato)copper(II) (Table I) do not show absorptions near 1130 cm⁻¹.

Of the five expected A₁ vibrational bands, four are observed in the Raman. The fifth band, ν_2 (observed at 1455 cm⁻¹ in the infrared spectrum), is probably masked by the asymmetric band at 1438 cm⁻¹.

The band near 1696 cm⁻¹ in the Raman (1685 in the infrared) we assign as a combination, $\nu_8 + \nu_9$. Many workers[1-6] have assigned the bands observed in this

Table V. Force Constants Based on Internal Coordinates^a

Description	Coordinate pair(s)^{b,c}	Value, mdynes/Å
CH stretching	$r_{56}r_{56}^a$	5.268
CN stretching	$r_{15}r_{15}$ and $r_{45}r_{45}$	5.36
CN–CN interaction	$r_{15}r_{45}$	1.45
NN stretching	$r_{12}r_{12}$ and $r_{34}r_{34}$	5.21
CN–NN interaction	$r_{15}r_{12}$ and $r_{45}r_{34}$	1.05
CN–NN interaction	$r_{15}r_{34}$ and $r_{45}r_{12}$	0.35
NN–NN interaction	$r_{12}r_{34}$	1.05
N–N stretching	$r_{23}r_{23}$	5.56
CN–NN interaction	$r_{15}r_{23}$ and $r_{45}r_{23}$	0.50
NN–NN interaction	$r_{12}r_{23}$ and $r_{34}r_{23}$	0.57
CH bend	$\rho\alpha_{156}\rho\alpha_{156}$ and $\rho\alpha_{456}\rho\alpha_{456}$	0.58
CH bend–CH bend interaction	$\rho\alpha_{156}\rho\alpha_{456}$	0.28
CN(str)–CH bend interaction	$r_{15}\rho\alpha_{156}$ and $r_{45}\rho\alpha_{456}$	−0.12
CN(str)–CH bend interaction	$r_{15}\rho\alpha_{456}$ and $r_{45}\rho\alpha_{156}$	−0.09
NCN bend	$\rho\alpha_{154}\rho\alpha_{154}$	1.44
CN(str)–NCN bend interaction	$r_{15}\rho\alpha_{154}$ and $r_{45}\rho\alpha_{154}$	0.13
NCN bend–CH bend interaction	$\rho\alpha_{54}\rho\alpha_{156}$ and $\rho\alpha_{154}\rho\alpha_{456}$	−0.22
NNN bend	$\rho\alpha_{215}\rho\alpha_{215}$ and $\rho\alpha_{345}\rho\alpha_{345}$	1.34
CN(str)–NNN bend interaction	$r_{15}\rho\alpha_{215}$ and $r_{45}\rho\alpha_{345}$	0.13
NN(str)–NNN bend interaction	$r_{12}\rho\alpha_{215}$ and $r_{34}\rho\alpha_{345}$	0.30
NCN bend–NNN bend interaction	$\rho\alpha_{154}\rho\alpha_{215}$ and $\rho\alpha_{154}\rho\alpha_{345}$	0.28
NNN bend–NNN bend interaction	$\rho\alpha_{215}\rho\alpha_{345}$	0.40
NNN bend	$\rho\alpha_{123}\rho\alpha_{123}$ and $\rho\alpha_{234}\rho\alpha_{234}$	1.39
NN(str)–NNN bend interaction	$r_{12}\rho\alpha_{123}$ and $r_{34}\rho\alpha_{234}$	0.35
NN(str)–NNN bend interaction	$r_{23}\rho\alpha_{123}$ and $r_{23}\rho\alpha_{234}$	0.25
NCN bend–NNN bend interaction	$\rho\alpha_{154}\rho\alpha_{123}$ and $\rho\alpha_{154}\rho\alpha_{123}$	0.15
NNN bend–NNN bend interaction	$\rho\alpha_{215}\rho\alpha_{123}$ and $\rho\alpha_{345}\rho\alpha_{234}$	0.28
NNN bend–NNN bend interaction	$\rho\alpha_{215}\rho\alpha_{234}$ and $\rho\alpha_{345}\rho\alpha_{123}$	0.15
NNN bend–NNN bend interaction	$\rho\alpha_{123}\rho\alpha_{234}$	0.50
CH out-of-plane wag	$(r_{56}\gamma_{6514})(r_{56}\gamma_{6514})$	0.297
All torsionals	$(r_{jk}\delta_{ijkl})(r_{jk}\delta_{ijkl})$	0.201
All torsional–torsional interaction	$(r_{jk}\delta_{ijkl})(r_{j'k'}\delta_{i'j'k'l'});\ i \neq i'$, etc.	−0.006

^{a} All other force constants are assumed to be zero. ^{b} $\rho = (RR')^{1/2}$ where R and R' are the equilibrium bond distances for the bonds ij and jk and define the related angle. ^{c} Subscripts refer to the position of the atoms in the ring. Number 6 refers to hydrogen.

that the fundamental bands at 3128, 1287, 1189, and 1079 cm⁻¹ are symmetric (species A₁), whereas those at 1438, 1025, 1009, and 702 cm⁻¹ are asymmetric (species B₁); the out-of-plane bands at 910 and 454

region as a fundamental. However, if a physically meaningful set of force constants is used, it is not possible to calculate a spectrum, in substantial agreement with that observed, in which one of the fundamental

Table VI. Raman Spectrum and Depolarization Ratios for Sodium Tetrazolate Monohydrate

Vibrational mode	Raman spectrum[a]	Depolarization ratio[b]
ν_1	3128 (m)[c]	0.331
	1696 (sh)	...
(H₂O)	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. [c] As defined in Table I.

vibrations is located near 1696 cm^{-1}. Thus the 1696-cm^{-1} band is probably not a fundamental. (The band at 1647 cm^{-1} in the Raman is due to water.) Depolarization ratios could not be measured for either the 1696- or the 1647-cm^{-1} band because of fluorescence between 1500 and 2800 cm^{-1}. Attempts to remove the fluorescing material by passing the aqueous solution of sodium tetrazolate through activated charcoal were unsuccessful.

The form of the normal modes was determined from the Cartesian displacement representation of the normal modes[24] as given in Table VII. The elements of the

Table VII. Normal Coordinate to Cartesian Coordinate Transformation Matrix T

Vibrational mode	Distribution[a,b]
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	$-0.042y_1 + 0.072z_1 - 0.151y_2 -$ $0.078z_2 + 0.151y_3 - 0.078z_3 + 0.042y_4 +$ $0.072z_4 + 0.014z_5$
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	$-0.092y_1 + 0.038z_1 + 0.034y_2 - 0.094z_2 +$ $0.034y_3 + 0.094z_3 - 0.092y_4 - 0.038z_4 +$ $0.086y_5 + 0.596y_6$
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. Number 6 refers to hydrogen. [b] The z axis is coincident with the C–H bond; the y axis is perpendicular to z and is in the plane of the ring; the x axis is perpendicular to the plane of the ring.

matrix T, when multiplied by the square root of the atomic mass, represent the relative movement of the atom in the x, y, and z direction during the vibration, where T is defined as the transformation from normal coordinates to mass-weighted Cartesian coordinates.

(24) J. H. Schachtschneider, Technical Report No. 263-62, Shell Development Co., Emeryville, Calif., 1962.

The vibrations may be described as follows: ν_1, ν_6, and ν_{10}(Table IV) correspond to a C–H stretch, C–H in-plane bend, and C–H out-of-plane wag, respectively. The other normal modes are complicated ring motions in which all atoms of the ring move and cannot be simply described as C–N stretch, N–N stretch, etc. The motions can be described roughly as follows; ν_2, ν_3, and ν_5 are symmetric ring deformations, ν_4 is a symmetric ring breathing model, ν_7, ν_8, and ν_9 are asymmetric in-plane ring deformations, and ν_{11} and ν_{12} correspond to an out-of-plane ring b bending, symmetric and asymmetric with respect to the C_2 axis, respectively. The remaining bands observed in the infrared spectrum (Table IV) are combination bands, except for those at 3300 and 1640 cm^{-1} which correspond to an O–H stretching and an O–H bending, respectively, for water. For all of the combination bands, the direct product of the representations for the combination pair yields a representation which is both infrared and Raman active. The combination frequencies calculated from the present assignment of fundamentals is in close agreement with the observed combination frequencies and substantiates the present assignment.

In this calculation the effects of hydrogen bonding due to the water of hydration were neglected, a good approximation since all vibrational modes due to hydrogen bonding occur below 200 cm^{-1}. Thus any interactions between these modes and the genuine modes for the tetrazole ion would be small and would affect the calculated frequencies by only a few reciprocal centimeters.

Some of the interaction constants are quite large. In many cases,[25] it is observed that an interaction constant is one-tenth that of the related diagonal force constants. The presence of an unshared pair of electrons on each nitrogen may explain the large magnitude of the interaction constants.

The calculated and observed frequencies agree to within 4% (average deviation 1.5%) except for ν_5 which was calculated to be 962 cm^{-1} as compared to an observed value of 1065 cm^{-1}. The agreement is not excellent but is reasonable. It seems unlikely that refinement of the force constants would substantially alter the present conclusions. A refinement of the potential constants would require further studies of the infrared and Raman spectra of isotopically substituted sodium tetrazolate and/or of related systems, and speculation concerning the magnitude of the potential constants should be deferred until further data are available.

The present vibrational analysis forces a reassessment of previous assignments of the infrared spectra of tetrazoles. For example, Holm and Donnelly[1] have interpreted the band at 664 cm^{-1} as a C–H out-of-plane bend, which would require a much smaller value of the force constant than 0.297 mdyne/Å, and seems unlikely, since this is already much smaller than that observed for the C–H out-of-plane bend in benzene and in the cyclopentadienide ion ($\simeq$0.4 mdyne/Å). Jonassen, et. al.,[2] Holm and Donnelly,[1] and Lefebre and Werner[26] have assigned the band at 1430–60 cm^{-1} as stretching of the N_2N_3 bond. The present vibrational

(25) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 57–59.

(26) R. J. W. Lefebre and R. L. Werner, *Australian J. Chem.*, 10, 26 (1957).

analysis shows, however, that all modes except those attributed to C–H motion include motion of all atoms of the ring.

Contact-Shift Studies, Delocalization Mechanisms, and Extended Hückel Calculations of Nickel(II)–Alkylamine Complexes[1a]

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Abstract: The proton nmr contact shifts of $[Ni(RNH_2)_6]^{2+}$ ($R = CH_3$, C_2H_5, $n\text{-}C_3H_7$) have been investigated in an attempt to extend our knowledge of unpaired spin delocalization mechanisms. The amino and alkyl protons are assigned in the nmr spectra of these complexes, and the contact shifts and hyperfine coupling constants are reported. A large upfield shift for the amino protons and a downfield shift for the alkyl protons were observed in all of the complexes studied. The nmr data indicate an attenuation in the magnitude of the contact shift as one proceeds down the chain from the nitrogen. This is in agreement with prediction for a σ delocalization mechanism. Molecular orbital calculations, using extended Hückel theory, were carried out on the ligands. The calculated electron spin density ratios, evaluated by using a Ψ^2 program for calculating electron density at a given nucleus, are compared with the experimental ratios. Justification for using only the ligand in these calculations is discussed and a method of averaging the rotational configurations of the amine is given.

The general theory and interpretation of nmr contact shifts have been extensively discussed in a previous publication from this laboratory[2] and in a recent review article.[3] One of the major problems in this area involves interpretation of the mechanism of spin delocalization onto the ligands. In most of the systems studied previously, the ligands are complex, and it often becomes difficult to sort out σ and π contributions to the delocalization mechanisms. This difficulty was demonstrated in a recent report[4] on the contact shifts of $[Ni(C_6H_5CH_2NH_2)_6]^{2+}$. Consequently, we chose relatively simple ligands to evaluate delocalization of unpaired spin density in a σ molecular orbital. If we can obtain a quantitative understanding of these simple systems, the more complex systems can then be attacked with greater confidence.

There have been several studies in which σ delocalization mechanisms have been reported to be the dominant mechanism. Happe and Ward[5] reported proton nmr contact shifts indicating a σ delocalization in nickel(II)–pyridine type complexes. Very recently, Eaton, *et al.*,[6] have investigated electron delocalization in σ systems in a series of substituted nickel(II) aminotroponiminates. Fessenden and Schuler have also investigated the esr spectra of some alkyl radicals.[7] These latter two studies are fundamentally different, however, from our study, since in the latter studies unpaired electron spin essentially in the π system is delocalized into the σ system *via* a hyperconjugative or some indirect $\pi \rightarrow \sigma$ mechanism.

The alkylamine–nickel(II) complexes, $[Ni(RNH_2)_6]^{2+}$ (where $R = CH_3$, C_2H_5, $n\text{-}C_3H_7$), offered us an opportunity to examine a σ delocalization mechanism in a complex where the metal–ligand bonding is essentially σ and the free ligand contains no π orbitals.

The recent success in calculating epr hyperfine coupling constants with an extended Hückel treatment, for some hydrocarbon σ radicals[8] and some σ radicals containing nitrogen and oxygen atoms,[9] prompted us to attempt to apply these calculations to nmr contact shifts. The nickel(II)–alkylamine complexes were thought to represent a relatively simple system for this initial attempt.

Experimental Section

Apparatus. **a. Nmr Spectra.** The nmr spectra were obtained on a Varian Model DP-60 spectrometer. All nmr spectra were measured relative to TMS as an internal standard.

b. Visible and Near-Infrared Spectra. All near-infrared and visible spectra were determined using a Cary recording spectrophotometer, Model 14RI.

(1) (a) Presented in part before the Division of Inorganic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) Abstracted in part from the Ph.D. thesis of R. Fitzgerald, University of Illinois, 1968; National Institutes of Health Predoctoral Fellow, 1966–1968.

(2) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

(3) D. R. Eaton and W. D. Phillips in "Advances in Nuclear Magnetic Resonance," Vol. I, J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, pp 103–148.

(4) R. J. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 2879 (1967).

(5) J. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(6) D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Am. Chem. Soc.*, **89**, 4040 (1967).

(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(8) R. S. Drago and H. Petersen, Jr., *J. Am. Chem. Soc.*, **89**, 3978 (1967).

(9) R. S. Drago and R. E. Cramer, to be published.