other such comparisons,[8,19,20] ions such as OH^-, Cl^-, Br^-, I^-, and N_3^- are expected to be at least as effective as CN^- as bridging ligands for inner-sphere electron transfer, such electron transfer presumably is occurring under the conditions of our reactions but is undetected.

The other mechanism of electron transfer, which might be expected to operate in these systems, is outer-sphere electron transfer between $Co(CN)_6^{4-}$ (generated by the equilibrium, $Co(CN)_5^{3-} + CN^- \rightleftarrows Co(CN)_6^{4-}$) and $Co^{III}(CN)_5X$, analogous to the outer-sphere oxidation of $Co(CN)_5^{3-}$ by $Co(NH_3)_6^{3+}$ and other cobalt(III) ammine complexes.[8] Such a reaction would also show up as a $Co(CN)_5^{3-}$-catalyzed conversion of $Co^{III}(CN)_5X$ to $Co(CN)_6^{3-}$ but with a CN^--dependent rate law, *i.e.*, $k_3[Co^{III}(CN)_5X][Co(CN)_5^{3-}][CN^-]$. The absence of any observed CN^- dependence permits upper limits to be placed upon the values of k_3 (listed in Table III) for each of the $Co^{III}(CN)_5X$ complexes. The values of these upper limits ($<2 \times 10^{-2}$ M^{-2} sec^{-1}) are much lower than the values of the corresponding rate constants (ranging from 5.2×10^2 M^{-2} sec^{-1} for $Co(NH_3)_5PO_4$ to 8×10^4 M^{-2} sec^{-1} for $Co(NH_3)_6^{3+}$) reported for the analogous CN^--dependent reactions between $Co(CN)_5^{3-}$ and various cobalt(III) ammine complexes.[8] The difference is unexpectedly large but in the direction expected on the basis of the observed dependence on the charge of the cobalt(III) complex.

Bis(1-substituted 5-tetrazolyl)nickel(II) Complexes

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Abstract: The complexes bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II) have been prepared and 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 and 14.7×10^3 cm^{-1}, and 8.33×10^3 and 14.7×10^3 cm^{-1}, respectively. The transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ was observed at approximately 25.0×10^3 cm^{-1} for bis(1-methyl-5-tetrazolyl)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 the 1-methyl complex and at 35.1×10^3 and 42.9×10^3 cm^{-1} for the 1-cyclohexyl complex. Bands were observed at 595, 456, and 298 cm^{-1} which may be attributed to the Ni–C bend, Ni–C stretch, and a 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 the 1-cyclohexyl complex. The observed magnetic moments, 2.90 and 2.98 BM, for the 1-methyl and 1-cyclohexyl complexes indicate two unpaired electrons.

The preparation of bis(1-methyl-5-tetrazolyl)nickel(II) in this laboratory was discussed in a preliminary communication.[1] Recently Beck and Fehlhammer[2] have prepared tetraphenylarsonium tetrakis(1-cyclohexyl-5-tetrazolyl)gold(III) by the reaction of tetraphenylarsonium tetrazidogold(III) with cyclohexylisonitrile in dichloromethane at 0°. The infrared spectrum of the 1-cyclohexyl-5-tetrazolyl ligand is essentially the same as that for 1-cyclohexyltetrazole.

The formation of a solid complex, tetrachlorobis(1-ethyltetrazole)platinum(IV), has been reported by Oliveri-Mandala and Alagna.[3] A number of complexes of various 1-substituted tetrazoles and several metal ions have been prepared and, except for the zinc complexes,[4] appear to be insoluble in all common solvents. The present work concerns the preparation of solid bis(1-substituted 5-tetrazolyl)nickel(II) complexes.

Experimental Section

Materials. Reagent grade chemicals were used throughout this investigation. The tetrazoles were prepared by the methods described previously for 1-phenyltetrazole[5] and for 1-methyl- and 1-cyclohexyltetrazole.[4]

The tetrazoles were purified by sublimation under reduced pressure. Purity was confirmed by comparing melting points and infrared spectra with previously reported values.[4,5]

Reagent grade diethyl ether (Et_2O) and tetrahydrofuran (THF) were purified by allowing them to reflux with lithium aluminum hydride under prepurified nitrogen and distilling off the ether. The fractions which boiled at 34.5 and 65°, 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 3 weeks. The acetone was subsequently refluxed with Drierite and distilled under nitrogen directly into the flask in which it was used.

Nickel(II) chloride and iron(III) chloride were prepared by dehydration of the hexahydrates by reaction with a slight excess of thionyl chloride[6] and then removing the remaining thionyl chloride under vacuum. Iron(II) chloride was prepared by reaction of chlorobenzene with iron(III) chloride.[7] Dichlorobis(triethylphosphine)nickel(II) was prepared by the reaction of triethylphosphine with an ethanolic solution of hydrated nickel(II) chloride.[8]

Analytical Methods. Nickel was determined by decomposing the complex (about 50–80 mg) with 30 ml of 6 *M* hydrochloric acid. The solution was heated to boiling to expel any hydrogen cyanide

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[1] L. L. Garber and C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, **88**, 4266 (1966).

[2] W. Beck and W. P. Fehlhammer, *Angew. Chem.*, **79**, 146 (1967).

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[5] F. Fallon and R. M. Herbst, *J. Org. Chem.*, **22**, 933 (1957).

[6] A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).

[7] P. Kovacic and N. D. Brace, *ibid.*, **6**, 172 (1960).

[8] K. A. Jensen, P. F. Nielson, and C. T. Pederson, *Acta Chem. Scand.*, **17**, 1115 (1963).

which formed and was evaporated nearly to dryness. To the residue (nickel(II) chloride) was added 20 ml of 1 *M* sulfuric acid. The solution was neutralized with concentrated ammonium hydroxide, and then 5 ml of concentrated ammonium hydroxide, 30 ml of water, 20 ml of standard cyanide ion solution, and 1 ml of potassium iodide (1 g/100 ml) as the indicator were added. The uncomplexed cyanide ion was titrated with a standard silver ion solution.

Iron was determined gravimetrically by using the procedure of Kolthoff and Sandell.[9]

Since the bis(1-substituted 5-tetrazolyl)nickel(II) complexes decompose in ammonium hydroxide to form cyanide ion (see Results), it is possible to determine the tetrazole content by determining the cyanide ion content once the nickel content is known. Cyanide ion was determined volumetrically by the procedure of Kolthoff and Sandell.[10]

Analyses for carbon, hydrogen, and nitrogen were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Purification of Nitrogen Gas. Matheson prepurified nitrogen was passed through a train of vessels containing, in order, sulfuric acid, barium oxide, and phosphorus pentoxide to remove water vapor and through a column containing copper wire at 500° and a column of Kieselguhr at 170° to remove any oxygen.

Preparation of 1-Methyl-5-tetrazolyllithium·0.5THF. To an excess of *n*-butyllithium (prepared under nitrogen by the reaction of equimolar amounts of lithium and *n*-butyl chloride at $-35°$) in 300 ml of freshly distilled, anhydrous THF was added 0.02 mole of 1-methyltetrazole under anhydrous conditions at $-50°$. The solution was stirred continuously for 1 hr at $-50°$, and 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-methyltetrazole.

Anal. Calcd for $LiC_2H_3N_4 \cdot 0.5THF$: C, 38.11; H, 5.60; N, 44.44. Found: C, 38.62; H, 4.92; N, 45.06.

Preparation of Bis(1-methyl-5-tetrazolyl)nickel(II). 1-Methyl-5-tetrazolyllithium·0.5THF was prepared as above but was used *in situ*. To about 0.02 mole of a THF suspension of the tetrazolyllithium compound at about $-50°$ was added about 0.01 mole of dichlorobis(triethylphosphine)nickel(II). The mixture, under nitrogen, was stirred for 2 hr and was allowed to come to room temperature and stand for about 4 hr. A finely divided green solid was separated either by centrifugation or filtration, under anhydrous and anaerobic conditions, washed repeatedly with anhydrous acetone, THF, and Et_2O, and allowed to dry in and was stored under an inert atmosphere. A yield of 80%, based on 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 allowed to react with the lithium compound at room temperature for 1 week. Extreme care must be exercised to ensure that the complex is not exposed to air or moisture. When wet the complex decomposes to give a yellow substance, but when dry the decomposition rate appears to be much slower and there is no formation of the yellow compound. The yellow compound could not be identified.

Anal. Calcd 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. Calcd for $Ni(C_2H_3N_4)_2 \cdot 2CH_3NO_2$: Ni, 16.9. Found: Ni, 17.1.

Preparation of Bis(1-cyclohexyl-5-tetrazolyl)nickel(II). The same procedure was used as described for $Ni(C_2H_3N_4)_2$ except that 1-cyclohexyltetrazole was substituted for 1-methyltetrazole and 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. Calcd 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 1 week. Filtration of the solution and suspension left only white 1-phenyl-5-tetrazolyllithium.

Attempted Preparation of Bis(1-methyl-5-tetrazolyl)iron(II). To a 0.02-mole suspension of 1-methyl-5-tetrazolyllithium was added 0.01 mole of anhydrous iron(II) chloride. After letting the suspension stand for 6 weeks, a very poorly defined orange compound was isolated. Because of the length of time required for preparation and lack of purity, this preparation was not repeated.

Reflectance Spectra. Reflectance spectra in the ultraviolet, visible, and near-infrared regions were obtained with a Beckman DK2 spectrophotometer equipped with a reflectance attachment. The samples were held in a 2 in. × 2 in. aluminum plate with a cylindrical bore (1 in. × $^1/_{16}$ in.). All samples were prepared with approximately two parts of magnesium oxide or silica to one part of complex and were forced into the sample holder and packed so that none of the complex would fall into the reflectance cavity. The samples were loaded in a drybox and kept under anhydrous conditions until the spectra were recorded. 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.

Magnetic Susceptibility Measurements. The Gouy method was used to obtain the magnetic moments at room temperature. An inert atmosphere was maintained throughout the measurements. $Hg[Co(SCN)_4]$ was used as a standard. The moments were corrected for the diamagnetism of the ligands by use of Pascal's constants.[11]

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. Care was taken to avoid contact with water vapor.

Results and Discussion

The complexes bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II) and the compound 1-methyl-5-tetrazolyllithium·0.5THF were prepared and characterized. The nickel complexes exhibit no detectable solubility in any common solvents. The lithium compound is insoluble in benzene, ether, and tetrahydrofuran. No attempt was made to find a solvent which would dissolve the lithium compound since the primary purpose of this investigation is the preparation and characterization of transition metal complexes of the tetrazolyl ion. The complexes decompose on heating without melting.

The $Ni(C_2H_3N_4)_2$ and $Ni(C_7H_{11}N_4)_2$ decompose in ammonia to give methanol and cyclohexanol, respectively, CN^-, and N_3^-. Methanol and HN_3 were identified by means of vapor phase chromatograms. Methanol and cyclohexanol were also identified by means of their nmr spectra. The cyanide ion was identified with standard qualitative and quantitative procedures. The agreement between the calculated and found analysis for cyanide indicates that cyanide ion is formed quantitatively. The compounds $Ni(C_2H_3N_4)_2$ and $Ni(C_7H_{11}N_4)_2$ also decompose in acidic solution but do not do so quantitatively. Only about 55% of the ring decomposes in $Ni(C_2H_3N_4)_2$ as determined by the cyanide analysis.

The reflectance spectra of $Ni(C_2H_3N_4)_2$ and $Ni(C_7H_{11}N_4)_2$ (Table I) are what would be expected for an octahedral or distorted octahedral spin-free nickel(II)

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(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p 320 ff.

(10) Reference 9, p 478 ff.

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

Table I. Spectral Assignments for $Ni(C_2H_3N_4)_2$ and $Ni(C_7H_{11}N_4)_2$

Complex	ν_1, cm^{-1}	Assignment
$Ni(C_2H_3N_4)_2$	8.06×10^3	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	14.7×10^3	${}^2A_{2g} \rightarrow {}^3T_{1g}(F)$
	$\sim 25.0 \times 10^3$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$
	30.9×10^3	Charge transfer
$Ni(C_7H_{11}N_4)_2$	8.33×10^3	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	14.7×10^3	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	$\sim 26.6 \times 10^3$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$
	$\sim 35.1 \times 10^3$	Charge transfer
	$\sim 42.9 \times 10^3$	Charge transfer

complex with *Dq* = 806 and 833 cm^{-1}, respectively. These *Dq* values compare with a *Dq* value of 850 and 1070 cm^{-1} for $Ni(H_2O)_6^{2+}$ and $Ni(NH_3)_6^{2+}$, respectively.[12,13] Thus the 1-methyl- and 1-cyclohexyl-5-tetrazolyl ligands form weaker complexes with nickel(II) than does water. The shoulders observed at approximately 25.0×10^3 and 26.6×10^3 cm^{-1}, respectively, would be the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions. From the energy-level diagram for $(3d)^8$, computed by Liehr and Ballhausen,[14] the d-d transitions for a regular octahedron should appear at $12.5\text{–}14 \times 10^3$ and $23\text{–}24 \times 10^3$ cm^{-1} for $Ni(C_2H_3N_4)_2$, while those for $Ni(C_7H_{11}N_4)_2$ should appear at $14\text{–}15 \times 10^3$ and $24\text{–}25 \times 10^3$ cm^{-1}. A charge-transfer band was observed at 30.9×10^3 cm^{-1} for $Ni(C_2H_3N_4)_2$. Fallon[15] observed no absorption below 43.4×10^3 cm^{-1} for a large number of 1-alkyltetrazoles. Thus the charge-transfer band should be a result of the transfer of an electron from the tetrazole ring to an e_g orbital. Two broad charge-transfer bands were observed for $Ni(C_7H_{11}N_4)_2$ at approximately 35.1×10^3 and 42.9×10^3 cm^{-1} and are probably due to electron transfer from a ligand to the e_g orbital and to a ligand π to π^* transfer, respectively.

The magnetic moments for $Ni(C_2H_4N_4)_2$ and $Ni(C_7H_{11}N_4)_2$ are 2.90 and 2.98 BM, respectively (Table II), and are sufficiently close to the spin-only value of 2.83 BM. The complexes have two unpaired electrons which is consistent with the electronic absorption spectra.

Table II. Magnetic Moments for $Ni(C_2H_3N_4)_2$ and $Ni(C_7H_{11}N_4)_2$

Compound	Temp, °C	Magnetic susceptibility χ_M[a]	Exptl moment, BM
$Ni(C_2H_3N_4)_2$	24.0	3479×10^{-6}	2.90
$Ni(C_7H_{11}N_4)_2$	22.5	3712×10^{-6}	2.98

[a] Units of χ_M are per mole.

The infrared spectra and vibrational assignments for 1-methyltetrazole, 1-methyl-5-tetrazolyllithium·0.5THF, and bis(1-methyl-5-tetrazolyl)nickel(II) are given in Table III. In the main, the features of 1-methyltetrazole are retained but with changes in intensities and slight shifts in position of the absorptions.

Table III. Infrared Spectra for 1-Methyltetrazole, 1-Methyl-5-tetrazolyllithium·0.5THF, and Bis(1-methyl-5-tetrazolyl)nickel (II)[a,b]

Genuine vibr mode	Tetrazole	$LiC_2H_3N_4$ 0.5THF	Ni-$(C_2H_3N_4)_2$	Assignment
	3400 (vw)	3400 (m)	3400 (m)	$\nu_7 + \nu_9 + \nu_{17}$
			3180 (m)	$\nu_5 + \nu_{10} + \nu_{22}$
ν_1	3135 (s)			Ring C–H stretch
ν_2	2980 (m)	2930 (vs)	2930 (vs)	Asym CH_3 stretch
ν_3		2880 (sh)	2890 (s)	Sym CH_3 stretch
		2830 (w)	2830 (s)	$2\nu_7$
		2250 (vw)	2250 (vw)	$\nu_9 + \nu_{13}$
ν_4		2150 (vs)	2150 (vs)	C≡N stretch
	1639 (vw)	1610 (w)	1610 (s)	$\nu_{11} + \nu_{20}$
ν_5	1496 (s)	1482 (m)	1496 (s)	Ring vibration
ν_6	1471 (vw)			Ring C–H bend
		1462 (s)		CH_2 bend in THF
ν_7	1422 (m)	1425 (s)	1425 (s)	Asym CH_3 bend
	1402 (w)	1382 (vw)		$\nu_{14} + \nu_{20}$
ν_8		1350 (s)	1348 (vs)	Sym CH_3 bend
ν_9	1279 (s)	1284 (vs)	1284 (vs)	Ring vibration
ν_{10}	1225 (m)	1220 (w)	1223 (w)	CH_3–N stretch
ν_{11}	1174 (vs)	1170 (w)	1182 (m)	Ring vibration
		1155 (vw)		$\nu_{18} + \nu_{19}$
ν_{12}	1113 (s)	1130 (w)	1125 (w)	Ring vibration
	1058 (m)		1055 (m)	$2\nu_{19}$
	1040 (w)			$\nu_{17} + \nu_{23}$
ν_{13}	973 (vs)	970 (vs)	955 (vs)	Ring vibration
ν_{14}	928 (m)	953 (vs)	925 (vs)	Ring vibration
ν_{15}	881 (vs)			Ring C–H out-of-plane wag
ν_{16}		855 (w)		Li–C stretch
			755 (w)	$\nu_{20} + \nu_{24}$
	719 (s)			$2\nu_{23}$
ν_{17}	678 (vs)	673 (s)	675 (vs)	Ring vibration
	658 (s)		660 (s)	$\nu_{13} - \nu_{23}$
ν_{18}		605 (s)		Li–C–bend
ν_{21}			595 (w)	Ni–C bend
ν_{19}	534 (s)	556 (m)	521 (m)	Out-of-plane ring bend
ν_{22}			456 (w)	Ni–C stretch
ν_{20}	476 (s)	437 (m)	437 (m)	Out-of-plane ring bend
ν_{23}	357 (m)	354 (sh)	337 (m)	CH_3–N skeletal vibration
ν_{24}			298 (s)	Ni–N stretch

[a] The symbols vs = very strong, s = strong, m = medium, w = weak, and vw = very weak. [b] Units are in cm^{-1}.

A vibrational analysis of the tetrazolate ion has been performed,[16] and vibrational assignments have been made. From these results the genuine modes of 1-methyltetrazole were deduced. The results for the tetrazolate ion indicate that aside from the ring C–H vibrations, the remaining genuine modes can be described best by total ring motion; *i.e.*, there are no unique C–N, N–N stretches, etc. The crystal structure of 1-methyltetrazole shows that all bond angles, both C–N and all N–N bonds in the ring, have approximately the same values[17] as were observed for the tetrazolate ion.[18] Thus the *F* matrix (potential energy) would be approximately the same as for the tetrazolate ion, and, since the Cartesian normal displacement coordinates, which depend upon the *F* matrix, determine the vibrational assignments, the ring probably vibrates as a whole in 1-alkyltetrazoles. The asymmetric CH_3 and symmetric CH_3 stretches are probably the ν_2 and ν_3 bands, respectively, and the asymmetric and symmetric

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

Genuine vibr mode	1-Cyclohexyl-tetrazole	$Ni(C_7H_{11}N_4)_2$	Assignment[a]
		3420 (s)	$1370 + 1350 + \nu_7$
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)		$\nu_4 + 337$
	1404 (w)		1054 + 337
	1366 (m)	1370 (m)	*
		1350 (m)	$900 + \nu_{10}$
	1344 (w)	1338 (w)	*
	1310 (m)	1302 (m)	*
	1266 (m)	1262 (s)	*
	1242 (w)	1241 (w)	*
		1215 (s)	$900 + \nu_{11}$
ν_3	1180 (sh)	1185 (w)	Ring vibration
	1167 (vs)	1163 (w)	*
	1138 (s)	1146 (w)	*
ν_4	1101 (vs)	1095 (w)	Ring vibration
		1078 (w)	$\nu_9 + 466$
	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)	$\nu_9 + 337$
	820 (s)	802 (sh)	*
		790 (s)	$466 + \nu_{11}$
	746 (s)		$\nu_3 - \nu_{10}$
	718 (vw)		$1266 - \nu_{10}$
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)	*
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.

CH_3 bends are then the ν_7 and ν_8 bands.[19] The CH_3–N stretch is probably ν_{10} and the CH_3–N skeletal vibration, ν_{23}.[19] The Ni–C stretch[20] in $Ni(CN)_4^{2-}$ is found at 543 cm^{-1} and the bend at 433 and 421 cm^{-1}, and the Fe–C stretch[21] 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 a Ni–N bond[22,23] by analogy to nickel–pentamethylenetetrazole and nickel–pyridine complexes.

The infrared spectra of 1-cyclohexyltetrazole and bis(1-cyclohexyl-5-tetrazolyl)nickel(II) are presented in Table IV. The vibrational modes due to the cyclohexyl substituent were determined by comparing the infrared spectrum of 1-cyclohexyltetrazole with those for cyclohexanol and cyclohexylamine. 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 very similar, and the bonding also should be similar.

The structures of $Ni(C_2H_3N_4)_2$ and $Ni(C_7H_{11}N_4)_2$ are probably polymeric. The tetrazole ring seems to be intact in the complex, if the over-all infrared spectrum is considered and since more than half of the 1-methyltetrazole is recovered when the complex is decomposed in acid. Since the ring is broken in concentrated ammonia between the 1 and 5 and the 3 and 4 positions, it appears that the 1,5 N–C and the 3,4 N–N bonds are labile and may be rather ionic.

Because nickel is probably six-coordinate (octahedral or tetragonal), 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. By working with framework molecular models only one arrangement seems possible: the two Ni–C and each pair of Ni–N bonds are *trans*, an infinite array is formed, and the structure is compatible with the insolubilities of the complexes. The 4-N and the 2- or 3-N would be bound to nickel.

Crystal structures have been determined for pentamethylenetetrazole iodine monochloride and dichlorobis(1-methyltetrazole)zinc(II).[24,25] 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, possibly is involved in the coordination of $Ni(C_2H_3N_4)_2$.

Acknowledgment. This work was supported by a grant (MH-07825) from the National Institutes of Health. The authors wish to thank Dr. C. Van Hill, Dow Chemical Company, for his help with the reflectance spectra.

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