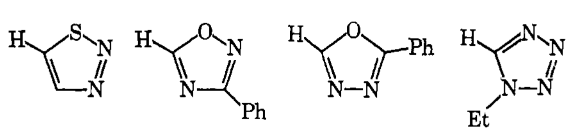

Figure 1. Half-time for exchange in 0.40 *N* piperidine in MeOD at 31° (substrates insoluble in D_2O and rates too fast for NaOMe–MeOD).

evident that there is an extraordinary rate enhancement when a proton is on carbon next to sulfur, suggesting that d–σ overlap is a major factor in stabilizing these anions. The greatest surprise comes from the discovery that both H_2 and H_5 in thiazole (IV) deprotonate at about the same rate and that H_5 of isothiazole (V) exchanges even faster. From a comparison of IV and V it would seem that the only important factor is the sulfur effect, and superficially it makes little difference whether the ring nitrogen is α or β to the carbon bearing the exchanging proton. This is contrary to LCAO–MO calculations[5] or even a simple consideration of inductive effects.

However, inductive and electronegative atom effects are important in these systems. Electron-withdrawing substituents (VIII) increase the isothiazole (V) exchange rate, whereas electron-releasing substituents (VI, VII) slow it down. Addition of an extra β nitrogen gives the thiadiazoles (IX and X) which deprotonate $10^{3.5}$ faster than IV and V, respectively; also thiophene does not exchange with 2 *M* NaOMe in boiling MeOD. This suggests that bases which do not contain sulfur will exchange if the model substrate contains: (1) additional electron-withdrawing substituents, (2) more electronegative atoms, (3) more powerful electron-withdrawing atoms such as oxygen, or (4) these groupings placed more closely to the exchanging protons. The correctness of this postulate is verified with some selected examples in Figure 1, and it is seen what combinations of these factors will give an exchange rate equivalent to that of X.

The remarkable fact that H_5 in isothiazole is ionized more readily than H_2 in thiazole is repeated in the thiadiazoles where H_5 in X (a model for isothiazole with an extra β nitrogen) deprotonates faster than H_2 in IX (a model for thiazole also with an extra β nitrogen) and in the thiadiazolium salts: 3-ethyl-1,2,3-thiadiazolium cation (a model for isothiazole with extra β-N-alkyl, positively charged) deprotonates at C-5 faster than the 3-ethyl-1,3,4-thiadiazolium cation (a model for thiazole with extra β-N-alkyl, positively charged) deprotonates at C-5 ($k_2 \times 10^{-5}$ l./mole sec.; 4.6 to 1.8[1]).

These exchange rates do not depend much on the solvent–base system (k_{H_2}/k_{H_5} for IV is 1.4 in NaOD–D_2O, 1.1 in NaOMe–MeOD, and 3.6 in KO-*t*-Bu–*t*-BuOD), thus lessening the possibility that the results may echo differences in steric effects, solvation effects, or electron-pair repulsion effects in the two molecular environments. We suspect these results may reflect a difference in the exact geometry (bond angles and bond lengths) of these heterocycles such as to increase the ease of d–σ overlap in the direction opposite to the nearest atom bearing a free electron pair in the plane of the ring, or they may reflect differences in some special multiatom overlap effect utilizing higher orbitals in the respective anions and the sp^2 electrons on the S and N. Experiments are being carried out to test these hypotheses.

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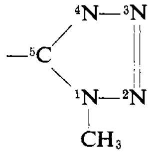
A Nickel–Carbon Bond in Bis(1-methyl-5-tetrazolyl)nickel(II)

Sir:

We report the preparation and some properties of bis(1-methyl-5-tetrazolyl)nickel(II), which has a nickel–carbon bond at the 5-carbon atom, $Ni(C_2H_3N_4)_2$, where $C_2H_3N_4^-$ is



1-Methyltetrazole, prepared as in our previous studies,[1] was added under dry nitrogen to *n*-butyllithium and anhydrous tetrahydrofuran (THF) at −50°, and a gray solid, presumed to be 1-methyl-5-tetrazolyllithium, separated out. If the solution was warmed, butane was evolved, as verified by mass spectrography. To about 0.02 mole of a THF suspension of the tetrazolyllithium at about −50° was added about 0.01 mole of dichlorobis(triethylphosphene)nickel(II).[2] The mixture 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 by centrifugation, washed with THF and acetone, and allowed to dry under a nitrogen atmosphere. A yield of 80% (based on the nickel) of bis(1-methyl-5-tetrazolyl)nickel(II), $Ni(C_2H_3N_4)_2$, was obtained. A very low yield of the compound was also obtained when anhydrous nickel chloride was used in place of the triethylphosphine complex.

Nickel was determined by the volumetric cyanide method[3] after the sample had been decomposed with 6 *M* HCl, evaporated to dryness, dissolved in a small amount of 2 *N* H_2SO_4, and then treated with concentrated ammonia. Because of fairly rapid decomposition in the atmosphere, satisfactory commercial C, H, and N analyses could not be obtained. However, the complex decomposes in ammonia to give CN^-, CH_3OH, and N_3^-, and thus the CN^- could be determined. The decomposition products were determined by means of

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vapor phase chromatograms and nmr spectra (for CH_3OH) and comparison with those of known samples of HCN, HN_3, and CH_3OH. To a sample in concentrated NH_3 was added a known excess of KCN, and the excess was titrated with a standard silver solution as in the Ni determination. From the percentage nickel and the known amount of added CN^-, the CN^- arising from the complex could be determined.

Anal. Calcd for $Ni(C_2H_3N_4)_2$: Ni, 26.1; CN^-, 23.2. Found: Ni, 26.3; CN^-, 23.4.

The tetrazolylnickel when wet decomposes rapidly in the atmosphere, but when dry decomposition is slow. The compound has appreciable solubility only in dimethyl sulfoxide in which a blue solution forms. Further studies of these solutions are in progress. If 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.

The tetrazolylnickel decomposes rapidly in concentrated NH_3 (see above) and in acid solutions, in which some HCN, HN_3, and CH_3OH are formed, but mostly the products are Ni^{2+} and 1-methyltetrazole. The complex decomposes more slowly in contact with neutral solutions. It explodes upon being heated in a flame.

Magnetic susceptibility was measured by the Gouy method, with $Hg[Co(SCN)_4]$ as a standard; μ_{eff} was 2.90 BM. The moment was corrected for the diamagnetism of the ligand by use of Pascal's constants. The spin-only value for $3d^8$ is 2.83.

The electronic spectrum of the solid was obtained by use of a Beckman, Model DK-2, spectrophotometer and diffuse reflectance attachment and showed absorptions at 8.06×10^3, 14.7×10^3, a shoulder at 25.0×10^3, and a large (charge transfer) band at 30.9×10^3 cm^{-1}. If the maximum, which gives rise to the shoulder, was between 27 and 28 $\times 10^3$ cm^{-1}, the spectral pattern would correspond to octahedral nickel, and the two d-d transitions would correspond to $^3A_{2g}-^3T_{2g}(F)$ and $A_{2g}-^3T_{1g}(F)$.

Infrared spectra were measured in Nujol and Fluorolube mulls and in KBr disks and were measured on a Unicam SP-200 spectrometer. Far-infrared spectra were measured in Nujol mulls between CsBr and polyethylene plates on a Perkin-Elmer Model 301 spectrometer. In the main, the features of the tetrazole are retained but with changes in intensities and position of the absorptions.

Several important features should be pointed out here. Absorptions at 590 and 485 cm^{-1} are present in the complex and not in the free tetrazole and may be attributed to the Ni–C–N bend and to the Ni–C stretch, respectively. The Ni–C stretch[4] in $Ni(CN)_4^{2-}$ is found at 543 and the bend at 433 and 421 cm^{-1}, and the Fe–C stretch[5] in $Fe(CN)_6^{4-}$ is found at 416 and the bend at 583 cm^{-1}. A band is found only in the complex at 2150 cm^{-1} which is some 20–50 cm^{-1} higher than the C–N stretch in first-row transition element cyanides, but is probably the C–N stretch. A band occurs at 298 cm^{-1} which can probably be attributed to an Ni–N bond[6,7] by analogy to nickel pyridine and pentamethylenetetrazole complexes.

It seems likely that the complex is polymeric because of the low solubility in most solvents, the probable presence of both Ni–C and Ni–N bonds, and the octahedral configuration, which seems likely for the nickel from the electronic spectrum. The tetrazole ring seems to be intact in the complex, if we consider the over-all infrared spectrum and the recovery of most of the free tetrazole, when the compound is decomposed in acid. Since the ring is broken in concentrated NH_3 between the 1 and 5 positions and the 3 and 4 positions to give cyanide ion and ultimately methanol and azide, it appears that the 1–5 N–C and 3–4 N–N bonds may be rather ionic. The 5–4 C–N bond must be much more like the bond in cyano complexes and less like the C–N in the free tetrazole.

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An Interesting Yield Increase in the Formation of Cyclic Acyloins

Sir:

The extensive use of the acyloin condensation, especially for the synthesis of medium rings, has stimulated surprisingly little systematic study.[1] Good evidence for the radical nature of the heterogeneous reaction has been provided, but this work has not been continued.[2,3] There is also one report of the optimum, reproducible yields of cyclic product in the medium ring series.[4] This work reported over-all yields of cyclic ketones based on diester and suggested the necessity of the present study.

It was our desire to obtain relative rates of cyclization for the dimethyl esters of the nine- to fourteen-carbon dicarboxylic acids. As a first step we determined the approximate length of time required for the complete disappearance of the ester. These results are given in Table I.

Table I. Time Required for the Complete Consumption of Ester in the Heterogeneous Acyloin Condensation

Ester (dimethyl)	Time, min
Nonanedioate	480
Decanedioate	180
Undecanedioate	165
Dodecanedioate	60
Tetradecanedioate	30

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