NMR STUDY OF THE METAL COMPLEXES OF 1,5-DIMETHYLTETRAZOLE AND 1,4-BIS-(1-METHYL-5-TETRAZOLYL)*n*-BUTANE

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(Received 4 May 1970)

Abstract – Complex compounds of 1,5-dimethyltetrazole and 1,4-bis(1-methyl-5-tetrazolyl)*n*-butane with silver and magnesium ions were studied in nitromethane and acetonitrile solution by the measurement of the donor proton chemical shifts as a function of donor-acceptor mole ratio. The stoichiometry of the 1,5-dimethyltetrazole-silver complex in nitromethane solutions was found to be[$(Tz)_2Ag$]⁺ and a solid complex ($Tz)_2AgClO_4$ was isolated. In the other cases, although evidence was obtained for the complexation reaction, the resulting complexes were quite unstable. The fact that magnitudes of the chemical shifts of the N-methyl and the C-methyl protons of the 1,5-dimethyltetrazole upon complexation were approximately the same may indicate that the coordinating site in the tetrazole ring is the 3-nitrogen.

INTRODUCTION

COMPLEX compounds of 1,5-disubstituted tetrazoles have been fairly extensively investigated in this laboratory[1]. Most of the studies have been carried out on



pentamethylenetetrazole (hereafter abbreviated as PMT) which forms addition compounds with Lewis acids, such as halogens and interhalogens[2] and with transition metal perchlorates[3] and halides[4]. Only in the case of PMT·ICl complex was the structure of the solid compound determined[5]. The results indicate that the tetrazole ring acts as a monodentate ligand and that the bonding occurs through the nitrogen atom in the 4-position. There does not seem to be any *a priori* reason for the 4-nitrogen to be exclusively the donor site, and it is quite

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possible that other tetrazole complexes may have a different structure or that the bonding site may be different in solutions.

The stabilities of the silver(1) complexes with substituted PMT[6] and with cyclopolymethylenetetrazoles [7] were determined potentiometrically in acetonitrile and in aqueous solutions. The stoichiometry of the complex ion is $Ag(Tz)_2^+$ and the pK values for the formation constant were found to be ~2. The inductive effects of the substituent groups or of the length of the hydrocarbon chain were rather small.

An attempt has been made to prepare complex compounds of bi-tetrazoles where chelating effects may be expected, and 1,1'-diphenyl-5,5'-bitetrazole was synthesized for this purpose [8]. Attempts to prepare a solid complex with copper(II) perchlorate were, however, unsuccessful and a spectrophotometric study of the bitetrazole-iodine system in 1,2-dichloroethane and in nitromethane solutions gave very little indication of complex formation.

The present study was undertaken in order to determine by NMR spectroscopy the complexing ability of the simplest disubstituted derivative, 1,5dimethyltetrazole, and to further investigate the donor properties of bitetrazoles. The former compound was selected because of the simplicity of its NMR spectrum which consists of two sharp resonance lines at 2.50 ppm for the C-methyl and 3.97ppm for the N-methyl protons with respect to tetramethylsilane.

EXPERIMENTAL

1,5-dimethyltetrazole

The compound was prepared by the method of Markgraf *et al.*[9]. 46 ml of benzenesulfonylchloride were added dropwise with stirring to an ice-cooled solution of 25 g acetone oxime in 342 ml of 1M aqueous sodium hydroxide solution. After this addition was complete, $23 \cdot 1$ g of sodium azide, dissolved in a minimum quantity of water, were added dropwise. The heterogeneous mixture was slowly warmed to room temperature and refluxed for 24 hr. The solvent was removed under vacuum and the residue was extracted several times with hot benzene in order to remove the tetrazole. The product was recrystallized twice from a benzene–ether solution and then sublimed under vacuum yielding about 3 g of white crystalline product (Yield 6–7 per cent). The melting point of the tetrazole was $71-73^{\circ}$ (lit [9] $72-73^{\circ}$).

1,4-Bis(5-tetrazolyl)n-butane

The compound was prepared by a combination of the methods described by Finnegan *et al.*[10] and by Satzinger[11]. To a freshly distilled 150 ml portion of dimethylformamide in a 1 l., 3 necked round bottom flask fitted with a stirrer, condenser and alcohol thermometer, was added 28·3 g of sodium azide followed by the slow addition of the catalyst, aluminum chloride (8 g). The temperature of the solution was held at 70° while 21·8 g of adiponitrile were added dropwise with stirring. The solution was held at this temperature overnight and then at 110° for 24 hr. The solvent was removed under reduced pressure. The solid residue was acidified with conc. HCl to a pH of ~2. It should be noted here that HN₃ is produced in the neutralization and, for this reason, this step should be carried out in a well ventilated hood. The mixture was allowed to air dry, and then the product was extracted with hot acetone followed by recrystallization from ethanol. The melting point was 201–203° (lit 204–205°[10], 202°[11]).

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NMR study of the metal complexes

Preparation of 1.4-bis(1-methyl-5-tetrazolyl)n-butane

The compound was prepared by the methylation of the 1,4-bis(5-tetrazolyl)*n*-butane[12]. To 36.6 g of the acid, 1,4-bis(5-tetrazolyl)*n*-butane, dispersed in 150 ml of water, was added dropwise 50% sodium hydroxide solution until the phenolphthalein end point was reached. The solution was warmed to 70°, and 40 ml of dimethylsulfate were added dropwise. Additional sodium hydroxide was added when needed to maintain the phenolphthalein end point. The mixture was stirred for 5 hr and then concentrated under vacuum to about 75 ml. The aqueous layer was extracted several times with 50 ml portions of 1,2-dichloroethane. The solid residue from the dichloroethane layer was then mixed with chilled acetone. A solid compound precipitated out which melted at 136°. The compound was purified by recrystallization from nitromethane, and the final product melted at 139–140° as reported by Cohen *et al.*[12]. The yield was about 30 per cent. *Anal.* Calcd. C. 43-23; H, 6-35; N, 50-42. Found C, 43-22; H, 6-38; N, 50-58.

Solvents and metal salts

Nitromethane was purified by percolation through a 20 cm column of Dowex 50W-X8 acid-form cation exchange resin. The eluent was refluxed over granulated barium oxide and then fractionally distilled. The center portions of the distillate was collected and stored in amber bottles. The boiling point of the product was 101° and the i.r. and the NMR spectra agreed with the published data.

Fisher Certified Reagent grade acetonitrile was dried for several days over molecular sieves prior to use.

Metal salts used in this investigation were of reagent grade and were dried before use.

Preparation of solutions

Stock solutions of the metal salts and of the respective tetrazoles were prepared by direct weighing of the components into a volumetric flask and adding the solvent to the mark. Solutions for NMR measurements were prepared by mixing required volumes of the stock solutions.

NMR measurements

The NMR spectra were obtained on a Varian A56/60D spectrometer. Tetramethylsilane was used as internal standard. Sweep calibration on the spectrometer was checked daily using the sideband technique. All data were collected at ambient temperature.

RESULTS AND DISCUSSION

The addition of silver perchlorate to a solution of 1,5-dimethyltetrazole in nitromethane produced a downfield shift of the N-methyl and the C-methyl proton resonances. The magnitude of the shifts is dependent on the tetrazole/silver ion mole ratio as well as on the total concentration of the reactants.

Two experiments were performed in order to determine the stoichiometry of the Ag⁺-Tz complex in solution. In one experiment, the concentration of the tetrazole was held constant at 0.130 M while the concentration of the silver ion was varied from 0.0130 to 1.17 M. The observed chemical shift, δ_{obs} , in all cases, was a weighted average of the chemical shift of the free tetrazole, δ_{Tz} , and of the pure complex $\delta_{AgTz_{H}}$.

$$\delta_{\rm obs} = \alpha \delta_{\rm Tz} + \beta \delta_{\rm AgTzn}$$

where α is the fraction of the tetrazole in the free state and β is the fraction of tetrazole in the complex. When the relative chemical shift $\Delta_{obs} = \delta_{obs} - \delta_{Tz}$ was plotted vs. Ag⁺/Tz mole ratio, a curve shown in Fig. 1 was obtained. Extrapolation of the arms of the curve obtained for the C-methyl resonance shows a

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Fig. 1. Relative chemical shift $\Delta = \delta_{obs} - \delta_{Tz}$ of the Δ C-CH₃ and \bigcirc N-CH₃ proton resonance vs. the silver perchlorate/1,5-dimethyltetrazole mole ratio in nitromethane.

definite break at 1:2 mole ratio of silver to tetrazole which indicates a stoichiometry of $[AgTz_2]^+$. The N-methyl resonance shifts give similar results. However, at high mole ratios the observed chemical shift of the methyl protons becomes obscured by the methyl resonance of the solvent at 4.32 ppm. The shape of the curve and the position of the break was found to be independent of tetrazole concentration.

In the second experiment the concentration of the silver was held constant at 0.101 M and the concentration of the tetrazole was varied from 0.0101 to 0.323 M. At concentrations greater than 0.203 M (corresponding to a mole ratio greater than two tetrazoles to one silver ion) the solutions became cloudy and precipitation occurred. When the observed relative chemical shift, Δ_{obs} , was plotted vs. the mole ratio of silver ion to tetrazole, a straight line was obtained over the tetrazole concentration range from 0.0101 to 0.203 M for both the C-methyl and N-methyl proton resonance.

The precipitate was isolated and recrystallized from nitromethane. At room temperature the precipitate appeared as transparent needles which, upon heating to about 40°, became white and opaque. The needles finally melt over a temperature range of 139–141°. Anal. Calcd. for $Ag(C_3H_6N_4)_2ClO_4$: C, 17.86; H, 3.00; N, 27.77. Found: C, 17.59; H, 3.12; N, 26.68.

The limiting chemical shifts were estimated to be 20.1 Hz for the C-methyl protons and ~ 17 Hz for the N-methyl protons. At attempt was made to determine the formation constant of the complex by calculating the relative fractions of bound and unbound tetrazole from the chemical shift with the assumption that the concentration of the 1:1 complex was negligible, but the resulting values were scattered over at least one order of magnitude. It may well be that there is a substantial amount of 1:1 complex and/or that the limiting shifts are in error.

Similar studies were carried out with magnesium(II) salts, and with similar results. Chemical shifts of N-methyl and C-methyl protons were observed upon addition of Mg(II) salts to solution of 1,5-dimethyltetrazole in nitromethane. The magnitudes of the shifts were proportional to Mg^{2+} concentrations with the limiting shifts being ~20 Hz for the C-methyl and ~16 Hz for the N-methyl protons. Plots of the chemical shifts vs. Mg^{2+}/Tz or Tz/Mg^{2+} mole ratios gave rather smooth curves, and it is difficult to estimate unambiguously the coordination number from these curves.

In order to check whether the chemical shift of the tetrazole protons could be due to electrolyte effect on the solution structure rather than to complexation, NMR spectra of the Tz-Ag⁺ system were obtained at different ionic strengths using tetrabutylammonium perchlorate. A series of solutions was prepared in which concentrations of the tetrazole and silver ions were held constant at 0.0249 and 0.0254 M respectively and the concentration of tetrabutylammonium perchlorate was varied from 0.0056 to 0.497 M. The resonance frequency of the Cmethyl and the N-methyl protons remained essentially constant with the difference between the two extreme concentrations of Bu_4NClO_4 being ~1 Hz. Likewise, the position of the 4.32 ppm solvent proton resonance was found to be independent of the tetrazole silver salt concentration. It is evident, therefore, that the chemical shifts of the tetrazole protons are due to the complexation reaction.

It was also of interest to us to investigate by this technique the complexing ability of a bitetrazole, 1,4-bis(1-methyl-5-tetrazolyl)*n*-butane (hereafter abbreviated BMTB). The NMR spectrum of this substance in nitromethane shows 3 peaks, a singlet at 4.0 ppm attributed to the $-CH_3$ group, a triplet at 3.0 ppm due to the outer $-CH_2$ - groups of the butane chain (those connected to the tetrazole ring), and a quintet at about 2.0 ppm due to the inner $-CH_2$ - groups of the butane chain.

The last two multiplets are of low intensity, and chemical shifts at concentrations possible in the solvents selected could not be measured with desired accuracy. The singlet at 4.0 ppm would be suitable for these studies but it is very close to the nitromethane proton resonance and was found to shift under this

peak during complexation. For these reasons the study was carried out in acetonitrile solutions. Both the bitetrazole and silver perchlorate show adequate solubilities so that solutions up to 0.1 M in the two components could be prepared, and the 4.0 ppm signal of the bitetrazole was not obscured by the solvent resonances.

Spectra of the BMTB-AgClO₄ system at various concentrations were obtained. The chemical shift, as in the case of 1,5-dimethyltetrazole, was concentration dependent, but the magnitude of the shift was much smaller with the limiting value approaching ~6 Hz for solutions of which the concentration of BMTB was held constant at 5×10^{-2} M and the concentration of AgClO₄ varied from 2×10^{-2} M to 5×10^{-1} M. This behavior is analogous to that found for the 1,5-dimethyltetrazole-silver system in acetonitrile in which the tetrazole concentration was held constant at 1×10^{-1} M and the concentration of the AgClO₄ varied from 1×10^{-2} M to 5×10^{-1} M, and this may reflect the competitive behavior of the solvent *vis-a-vis* silver ions. It should be noted that, while in general, acetonitrile does not act as a strong donor, it does form fairly stable complexes with silver ion.

In order to test for possible chemical shifts due to electrolyte effect, spectra of BMTB were obtained in the presence of varying amounts of sodium perchlorate $(1 \times 10^{-2} \text{ to } 1 \times 10^{-1} \text{ M})$. The chemical shift of the 4.0 ppm resonance was found to be negligible. A plot of the 4.0 ppm resonance of tetrazole vs. Ag⁺/Tz mole ratio for both the BMTB and 1,5-dimethyltetrazole systems is shown in Fig. 2. It is seen that the plot does not show any readily apparent discontinuities and that the shift approaches a limiting value of ~6 Hz. While the extrapolation of the two branches of the curve shows an intersection of $2\text{Ag}^+/1$ BMTB mole ratio, it should be realized that this mole ratio may be fortuitous and additional experimental evidence will be necessary before the nature of the BMTB-Ag⁺ complex is completely ellucidated.

In all previous complexation studies involving 1,5-disubstituted tetrazoles as ligands, with one exception, the latter behaved as a unidentate ligand[1]. Only the insoluble polymeric pentamethylenetetrazole complexes with transition metal halides gave indirect evidence of tetrazole ring activity as a bridging ligand [4]. It is interesting, therefore, to establish the coordination site in the tetrazole ring. Crystal structure of the solid pentamethylenetetrazole–1C1 compound showed that the donor site is the 4-nitrogen. It is entirely possible, however, that different donor site may be active in solutions and/or with other acceptors. In fact, on a stereochemical basis, it is difficult to visualize the formation of the hexa-coordinated (PMT)₆M^{II}(ClO₄)₂ complexes[3] if the donor site was located at the 4-nitrogen.

It was seen above that the chemical shifts of the C-methyl and the N-methyl protons upon complexation in nitromethane solution are fairly close in value (~ 20 Hz and ~ 16 Hz respectively) which seems to indicate that the complexation occurs through the 3-nitrogen of the tetrazole ring. If the complexation occurred through the 2-nitrogen the coupling would occur through three atoms for the C-methyl proton and five atoms for the N-methyl protons. The opposite case would occur if the coordination site was the 4-nitrogen. In either event it would be expected that the chemical shifts for the N- and C-methyl proton resonances would be quite different. Although on the basis of this evidence one cannot con-



Fig. 2. Relative chemical shifts $\Delta = \delta_{obs} - \delta_{Tz}$ for the N-CH₃ resonance of the tetrazole vs. the mole ratio Ag⁺/Tz. Upper curve, 1,5-dimethyltetrazole-AgClO₄. Lower curve, 1,4-bis(1-methyl-5-tetrazolyl)*n*-butane-AgClO₄ in acetonitrile.

clude unambiguously that the coordination site is definitely the 3-nitrogen, this seems to be the most likely explanation of the present results.

Acknowledgement – This work was supported by a Research Grant NS69061 from the National Institutes of Health. R. H. E. gratefully acknowledges a predoctoral fellowship from the U.S. Public Health Service.