Steric Effects in Coordination of 1,1,1-Tris(dimethylaminomethyl)ethane and of 1,1,1-Tris(monomethylaminomethyl)ethane.[1] I. Zinc(II) Complexes

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Abstract: Steric effects in coordination of the new tripod ligand 1,1,1-tris(dimethylaminomethyl)ethane (TTN) and of 1,1,1-tris(monomethylaminomethyl)ethane (TSN) have been investigated by the preparation and characterization of their zinc chloride and zinc bromide complexes. The stereochemistry of the complexes has been established on the basis of data from ^{1}H nuclear magnetic resonance (nmr) spectroscopy, infrared spectroscopy, and complementary physical-chemical studies. The complexes of TSN have a cage-like structure consisting of three fused six-membered chelate rings and a pentacoordinated zinc atom due to the sterically unhindered tridentate behavior of TSN. In contrast, the complexes of TTN have only one six-membered chelate ring and a tetracoordinated zinc atom due to the sterically controlled bidentate behavior of TTN. The chelate ring is in a frozen pseudochair conformation and yields strikingly similar ^{1}H nmr data to purely organic structurally analogous nitrogen-containing heterocycles. This indicates that the zinc(II) nucleus, though chemically different from the carbon atom, does not produce any conformational change in these systems.

The secondary and tertiary N-methyl-substituted derivatives, 1,1,1-tris(monomethylaminomethyl)ethane (TSN for "secondary" nitrogen) and 1,1,1-tris(dimethylaminomethyl)ethane (TTN for "tertiary" nitrogen), of the primary tridentate amine 1,1,1-tris(aminomethyl)ethane (TPN) afford a uniquely simple series of ligands for a systematic investigation of the role of steric effects in coordination. TPN, TSN, and TTN are typical examples of the so called tripod ligand and can be represented by the general structure I, Figure 1. They differ structurally from the extensively studied tripod ligands such as tris(2-aminoethyl)amine (tren) and its hexamethyl derivative tris(2-dimethylaminoethyl)amine (trenMe), represented by structure II,[2] Figure 1. TPN, TSN, and TTN are potentially tridentate and contain only peripheral functional atoms. Chelation will give rise to the formation of fused six-membered chelate rings. On the other hand, tren and trenMe are potentially quadridentate and contain, in addition to three peripheral functional atoms, an apical internal functional atom. If the apical atom actually participates in coordination, chelation gives rise to the formation of five-membered chelate rings. If the apical atom does not take part in coordination, then eight-membered chelate rings are formed. It would appear[2] that the apical atom is indeed coordinated. This is in agreement with the generally accepted postulate that, in chelated systems containing only single bonds, a four-membered ring is less stable than a five-membered one, which is more stable than a six-membered ring. Rings containing seven and eight atoms are progressively less favorable.

Measurement of stability constants of the transition metal complexes of tren[3a] and of TPN[3b] in aqueous solution gives strong support to the statement that "it seems impossible to build up fully effective tridentate chelate ligands with only peripheral functional atoms."[4] However, the polynucleating ability of the potentially tetradentate primary amine, tetra(aminomethyl)methane, has been reported[5] and may indicate a different type of coordinating role for ligands of this type. On progressive N-methyl substitution, the coordinating ability of a series of N-methylated ethylenediamines toward copper(II) has been found to decrease due to the increasing steric effect.[6] Thus it appeared that the preparation of transition metal complexes of TSN and TTN might well prove to be a difficult but interesting challenge.

TSN was initially prepared by Laube, *et al.*,[7] and employed in the synthesis of a monophosphorus bicyclic aminophosphine, a number of its derivatives, and its arsenic analog. Unusual bidentate donor properties of the phosphorus compound were observed with diborane. The preparation of TTN has not previously appeared in the literature.

We now wish to report the preparation and the characterization of TTN and of the zinc chloride and bromide complexes of both TSN and TTN. Zinc chloride and bromide were the salts of choice on the basis that the "well-behaved" zinc atom would allow a true evaluation of the influence of steric effects in the chelating ability of TSN and TTN.

Experimental Section

Preparations of the Ligands. TSN and TTN were both prepared by a modification of Van Alphen's method[8] as follows. 1,1,1-Tris-

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(1) Abstracted from a portion of a thesis which is to be submitted by W. J. Kasowski to the University of Illinois in partial fulfillment of the requirements for the Ph.D. degree.

(2) (a) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, 1, 222 (1966); (b) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (c) *ibid.*, **5**, 1150 (1966); (d) M. Divaira and P. L. Orioli, *ibid.*, 6, 955 (1967); (e) L. V. Interrante, *ibid.*, 7, 943 (1968); (f) M. Ciampolini, *Chem. Commun.*, 47 (1966).

(3) (a) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 963 (1950); (b) G. Anderegg, *ibid.*, **45**, 1303 (1962).

(4) G. Schwarzenbach, *Advan. Inorg. Chem, Radiochem.*, **3**, 275 (1961).

(5) (a) R. W. Oehmke and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 27, 2199 (1965); (b) L. J. Zompa and R. F. Bogucki, *J. Am. Chem. Soc.*, **88**, 5186 (1966).

(6) S. Erhardt and D. W. Meek, *Inorg. Chem.*, **4**, 587 (1965).

(7) B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton, and J. G. Verkade, *ibid.*, 6, 173 (1967).

(8) J. Van Alphen, *Rec. Trav. Chim.*, **57**, 265 (1938).

Table I. ^1H Nuclear Magnetic Resonance Data for TSN, $TSNZnCl_2$, and $TSNZnBr_2$[a]

Proton	Field strength, Mc	TSN	$TSNZnCl_2$	$TSNZnBr_2$	IR[b]
$-(CH_2)-$	60	7.60	7.27	7.28	6
	100	7.54	7.20	7.22	6
$-N-CH_3$	60	7.70	7.44	7.46	9
	100	7.65	7.38	7.41	9
$-N-H$	60	8.54 (slight broadening)			
	100		Triplet	Triplet	3
			7.06	7.05	
		8.51 (slight broadening)	7.59	7.58	
			8.12	8.11	
			J_{H-N} = 53 cps	J_{H-N} = 53 cps	
$-C-CH_3$	60	9.22	9.03	9.04	3
	100	9.19	9.02	9.03	3

[a] In τ units (ppm relative to TMS). [b] IR = proton integration ratio.

(bromomethyl)ethane was prepared in 72–80% yield by converting 1,1,1-tris(hydroxymethyl)ethane to 1,1,1-tris(benzenesulfonylmethyl)ethane in 95% yield and causing the triester to react with NaBr in ethylene glycol according to a modification of Herzog's method.[9] This approach provided a much cleaner and more economical route to the tribromide than the PBr_3 method of Backer and Schurinck.[10]

A solution of 108 g (0.35 mole) of 1,1,1-tris(bromomethyl)ethane in 250 ml of anhydrous ethyl alcohol in a 1-l. glass-lined Magne Dash "floor-model" autoclave was cooled to 0°. Anhydrous dimethylamine, DMA (100 g, 2.22 moles), as received in sealed bottles, was cooled to 0° and added to the reaction mixture. An O-ring was inserted and the top of the autoclave secured with a torque wrench. The reaction mixture was stirred and heated at 160° for 10 hr. The cooled reaction mixture was diluted with 500 ml of distilled water and was then neutralized with dilute hydrochloric acid. The neutralized mixture was filtered, washed with ethyl ether to remove any neutral impurities, and concentrated under reduced pressure. When the concentrate was made basic with potassium hydroxide, crude TTN was liberated as an oily top layer. This was decanted and dissolved in ethyl ether. The basic aqueous solution was subsequently extracted with ethyl ether and the extracts added to the main solution. The ethereal mixture was filtered and dried over KOH. The dried mixture was distilled under reduced pressure and the distillate redistilled over barium oxide, giving pure 1,1,1-tris(dimethylaminomethyl)ethane (TTN), distilling at 33–34° (0.10 mm) or 49° (5 mm). The refractive index was 1.4481 at 26.0°. The yield was 56.6 g, 0.28 mole, or 80%. *Anal.* Calcd for $C_{11}H_{27}N_3$: C, 65.61; H, 13.52; N, 20.87. Found: C, 65.93; H, 13.39; N, 20.49.

1,1,1-Tris(monomethylaminomethyl)ethane (TSN) was prepared in the same way by reaction of 99.0 g (0.32 mole) of 1,1,1-tris(bromomethyl)ethane with anhydrous methylamine (MMA) (89.6 g, 2.89 moles, a threefold excess) at 170° for 10 hr. This gave 33.1 g, 0.21 mole (a 65% yield), of pure TSN distilling at 38–39° (8 mm) and having a refractive index of 1.4565 at 26.0°.

Preparation of the Zinc Chloride and Zinc Bromide Complexes of TSN and TTN. The complexes were prepared by the following general method. A solution of 0.010 mole of the freshly distilled triamine in 10 ml of anhydrous ethyl ether was added to 0.010 mole of the appropriate anhydrous zinc halide dissolved in a mixture of 30 ml of absolute ethyl alcohol and 10 ml of anhydrous ethyl ether. The clear colorless solution was heated to reflux, 35 ml of solvent was distilled off, and the remaining solution was allowed to cool slowly. The white crystals which deposited were collected, washed with anhydrous ethyl ether, and dried under vacuum over P_2O_5. Recrystallization was effected from either a mixture of anhydrous ethyl ether and chloroform, or from absolute ethyl alcohol.

Physical Measurements. The molecular weight of the complex $TTNZnCl_2$ was determined in chloroform and acetonitrile. Molecular weights of the complexes in the vapor state were measured by mass spectrometry and the first appearance potentials were recorded.

Elemental analyses were performed by Mr. J. Nemeth and his assistants in the University of Illinois Microanalytical Laboratory.

Melting points were taken in an open capillary on a Gallenkamp melting point apparatus and are uncorrected.

Conductivity values were obtained by use of an Industrial Instruments Inc. Model RC-16B2 conductivity bridge and a cell with a constant of 0.1388 cm^{-1}. The measurements were made at 26.0°, employing 10^{-3} *M* solutions.

Infrared spectra of the complexes in KBr disks and the free ligands in CCl_4 were obtained on a Perkin-Elmer 521 spectrophotometer.

The ^1H nmr spectra, relative to TMS, of the complexes in $CDCl_3$ and the free ligands in CCl_4 were observed at 60 and 100 Mc on Varian A-60 and HA-100 instruments, respectively.

Results and Discussion

The Ligands TSN and TTN. The ^1H nmr data illustrate the structural simplicity and confirm the symmetrical tripod geometry of TSN and TTN.

TSN has four different sets of equivalent protons, $-(CH_2)-$, $-N-CH_3$, $-N-H$, and $-C-CH_3$, which give rise to four single absorption bands (Table I). The slight broadening of the $-N-H$ signal may arise from the electric quadrupole moment of the nitrogen nucleus and from unresolved splitting due to the neighboring $-(CH_2)-$ and $-N-CH_3$ protons.

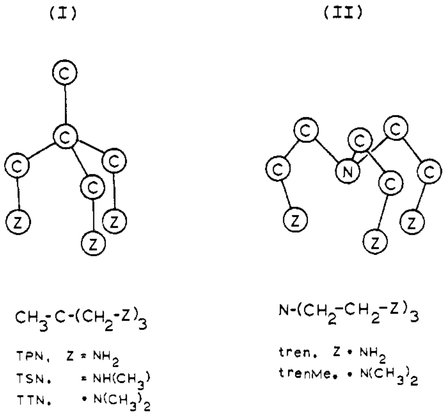

Figure 1. General structures of the tripod ligands of the types $CH_3-C-(CH_2-Z)_3$ and $N-(CH_2-CH_2-Z)_3$.

TTN has three different sets of equivalent protons, $-(CH_2)-$, $-N-CH_3$, and $-C-CH_3$, which give rise to three single absorption bands (Table II). It is of interest that in the case of TTN the $-(CH_2)-$ absorption appears at higher field than the $-N-CH_3$ absorption, but in the case of TSN, it appears at lower field. The upfield shift of the methylene absorption that accompanies complete N-methylation most probably re-

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(9) H. L. Herzog, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 753.

(10) H. J. Backer and H. B. J. Schurinck, *Rec. Trav. Chim.*, **50**, 921 (1931).

Table II. ^1H Nuclear Magnetic Resonance Data for TTN, $TTNZnCl_2$, and $TTNZnBr_2$[a]

Proton	Field strength, Mc	TTN	$TTNZnCl_2$	$TTNZnBr_2$	IR[b]
Equatorial $-(CH_2)-$ of the AB system in the six-membered chelate ring	100 (bands 1 and 2)		Doublet	Doublet	
			6.89	6.86	0.8
			7.02	6.97	1.2
			J_{11} = 13 cps	J_{11} = 13 cps	
			Δ(ae) = 0.54	Δ(ae) = 0.64	
Equatorial $-N-CH_3$ of six-membered chelate ring	100 (band 3)		7.29	7.27	6
			Δ(ae) = 0.03	Δ(ae) = 0.06	
Axial $-N-CH_3$ of six-membered chelate ring	100 (band 4)		7.31	7.33	6
Axial $-(CH_2)-$ of the AB system in the six-membered chelate ring	100 (bands 5 and 6)		Doublet	Doublet	
			7.44	7.47	1.2
			7.57	7.60	0.8
			J_{11} = 13 cps	J_{11} = 13 cps	
$-N-CH_3$ of free amine group	60	7.77			18
	100 (band 7)		7.66	7.65	6
$-(CH_2)-$ of free amine group	60	7.83			6
	100 (band 8)		7.84	7.83	2
$-C-CH_3$	60	9.13			3
	100 (band 9)		8.66	8.66	3

[a] In τ units (ppm relative to TMS). [b] IR = proton integration ratio.

flects an increased contribution to the diamagnetic inductive effect provided by the substitution of the secondary amine hydrogen atom with the methyl group.

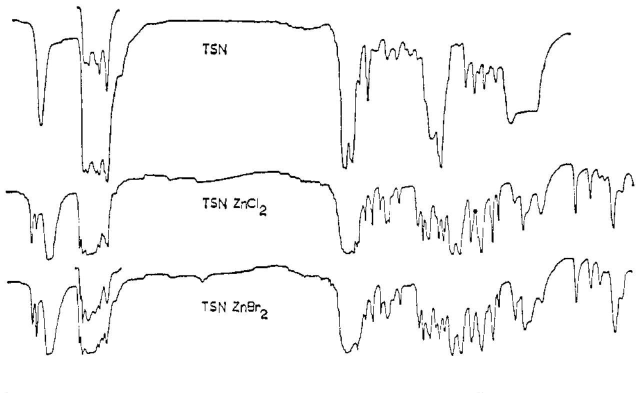

Figure 2. Infrared spectra of TSN, $TSNZnCl_2$, and $TSNZnBr_2$.

The symmetrical tripod geometry of TSN and TTN allows potentially tridentate behavior. However, it was recognized that steric conditions about the central metal atom, or the coordination number preference of the central metal atom, might prove so demanding that the ligands might be forced to act in a bidentate or even monodentate manner. This presented the possibility of free or uncoordinated amine groups. In the case of alkyl-substituted amines infrared spectroscopy provides a rapid qualitative technique diagnostic for the presence of the free amine group. Studies of organic bases containing the $-NCH_3$ group[11] show that the medium to strong bands in the 2800-cm^{-1} region, believed to be characteristic of the C–H stretching vibration of the free $-NCH_3$ group, disappear completely or partially on coordination to a metal atom or on salt formation. The more complete the disappearance, the greater is the extent of delocalization of the nitrogen lone-pair electrons.

The infrared spectra of TSN and TTN, Figures 2 and 3, show groups of three strong bands in the region 2880–2750 cm^{-1} that arise from the free $-NCH_3$ group. The relative intensity of the bands increases with decreasing wave number. Analysis of these bands in the infrared spectra of the $ZnCl_2$ and $ZnBr_2$ complexes of TSN and TTN provides valuable insight into the chelating behavior of the ligands.

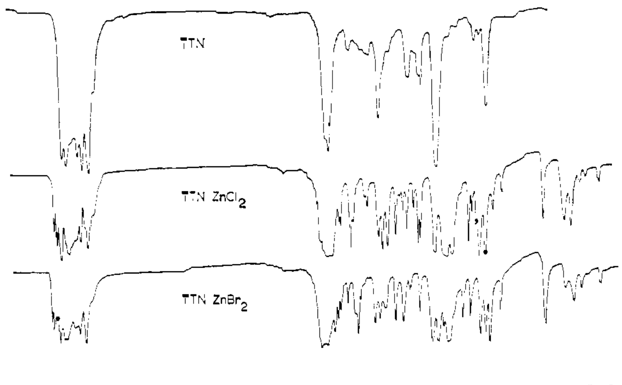

Figure 3. Infrared spectra of TTN, $TTNZnCl_2$, and $TTNZnBr_2$.

Complexes $TSNZnCl_2$, $TSNZnBr_2$, $TTNZnCl_2$, and $TTNZnBr_2$. The zinc chloride and bromide complexes of TSN and TTN have the general formula $LZnZ_2$. All of the complexes are air stable and soluble in typical organic solvents such as chloroform, acetonitrile, and nitromethane. Their solubility in straight-chain hydroxylic solvents decreases progressively from *n*-butyl alcohol to methyl alcohol. They are insoluble in water. The complexes all melt without decomposition and can be sublimed.

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(11) (a) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958); (b) J. R. Braunholz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppàrd, *ibid.*, 2780 (1958); (c) D. A. Baldwin and G. J. Leigh, *ibid.*, *A*, 1431 (1968).

Table III. Analytical and Physical Data for the Zinc Chloride and Bromide Complexes of TSN and TTN

Complex		$TSNZnCl_2$	$TSNZnBr_2$	$TTNZnCl_2$	$TTNZnBr_2$
Color		White	White	White	White
Mp, °C		167–169	163–165	128–130	122–124
Molar conductance, mho cm.^{2}/mole, at 26.0° in A ($CHCl_3$) and B (CH_3NO_2)		A nc[a] B 2.4	nc 4.5	nc 16.4	nc 20.4
First appearance potential, eV		15.0	13.5	16.5	14.0
Mol wt calcd for monomer		295.55	384.46	337.63	426.55
Found by mass spectra		304–294 pp[b]	388–382 pp	344–336 pp	432–424 pp
Found in $CHCl_3$				319	
Found in CH_3CN				300	
Elemental analysis (calcd for monomer)	% C calcd	32.51	24.99	39.13	30.97
	found	33.06	25.12	39.44	30.74
	% H calcd	7.16	5.51	8.06	6.38
	found	7.19	5.44	8.01	6.49
	% N calcd	14.22	10.93	12.44	9.85
	found	14.08	11.00	12.00	9.72
	% Zn calcd	22.12	17.00	19.36	15.33
	found	21.90	16.80	19.38	15.40
	% X calcd	23.99	41.57	21.01	37.47
	found	24.13	41.72	20.89	37.29

[a] nc = nonconductor. [b] pp = parent peak pattern region.

The data of Table III show that the complexes are monomeric covalent molecules. They are nonelectrolytes in chloroform. In the presence of the much stronger donor solvent, nitromethane, slight dissociation occurs. It is noted that this dissociation approximates only to 3.0 and 5.6% for $TSNZnCl_2$ and $TSNZnBr_2$, respectively, but increases by about fivefold for the corresponding TTN complexes. In much the same way, the other physical data such as melting points, first appearance potentials, infrared spectra, and ^1H nmr spectra reflect both the great similarity between the two complexes of a single ligand and the striking differences between the complexes of TSN and those of TTN. This trend in physical properties thus strongly suggests that the complexes of a particular ligand are structurally similar, but that the complexes of TSN are structurally different from those of TTN.

The coordination number and most probable geometry of the complexes were established on the basis of infrared and ^1H nmr data. The infrared spectra (Figure 2) of $TSNZnCl_2$ and $TSNZnBr_2$ are almost identical. Similarly, the infrared spectra (Figure 3) of $TTNZnCl_2$ and $TTNZnBr_2$ show very close agreement. However, there are important differences between the spectra of the $TSNZnX_2$ and the $TTNZnX_2$ complexes. A comparison of the 2800-cm^{-1} region of each complex with that of the corresponding free ligand reveals that in the $TSNZnX_2$ series the group of three bands suffers a large loss in intensity, and the relative order of intensity appears opposite to that exhibited by the free ligand. On the other hand, in the $TTNZnX_2$ series, though the group of three bands suffers some loss in intensity, the relative order of intensity remains unchanged from that exhibited by the free ligand. On this basis, it was tentatively assumed that TSN was behaving as a tridentate chelate, whereas TTN was behaving most probably as a bidentate chelate with one amine group uncoordinated. Hence, in the complexes $TSNZnX_2$ and $TTNZnX_2$, the zinc atom will possess coordination numbers of five and four, respectively, with corresponding distorted trigonal bipyramid or tetragonal pyramid and tetrahedral coordination geometries.

^1H nmr studies of the complexes provide proof for the correctness of the preliminary structural assignments.

In the $TSNZnX_2$ complexes, if it is assumed that the zinc atom has a coordination number of five as illustrated in Figure 4, and that in solution at room temperature the internal motions of the halogen atoms are sufficiently rapid so as to make the chemical environment at each nitrogen atom equivalent, a nmr spectrum closely resembling that of the free ligand would be predicted. However, on coordination, the delocalization of the nitrogen lone-pair electrons in the direction of the zinc atom may give rise to a general deshielding of the $-(CH_2)-$, $-NCH_3$, and $-NH$ protons and result in the downfield shift of these absorptions relative to their positions for the free ligand. On the basis of proximity to the nitrogen atom, the $-NH$ proton may be expected to show the largest relative downfield shift.

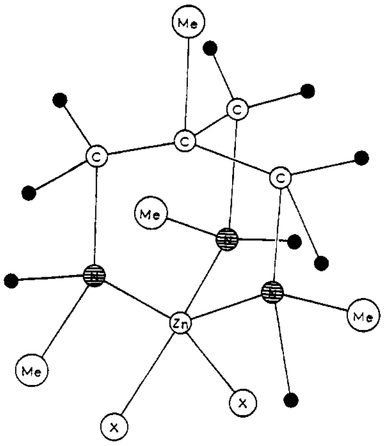

Figure 4. Structure of the $TSNZnX_2$ complexes: ● = hydrogen atom.

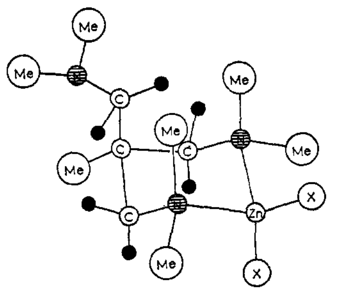

Figure 5. Structure of the TTNZnX$_2$ complexes: ● = hydrogen atom.

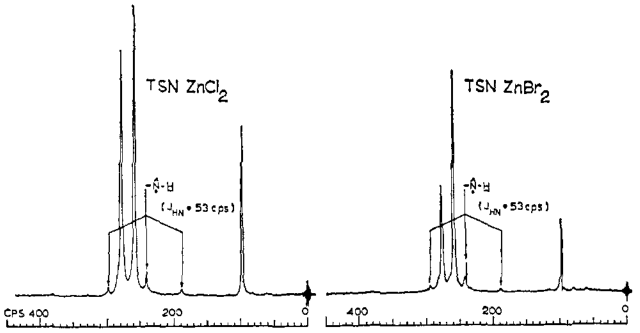

Figure 6. ^{1}H nmr spectra of TSNZnCl$_2$ and TSNZnBr$_2$ at field strength of 100 Mc and sweep width of 1000 cps.

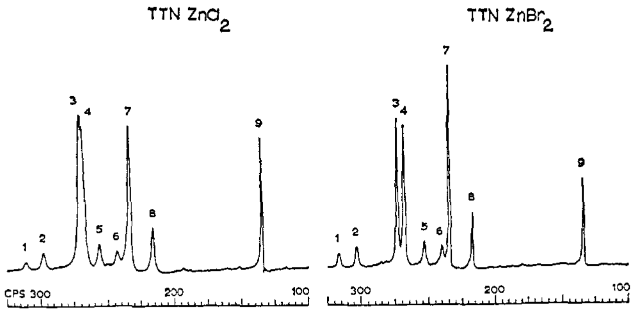

Figure 7. ^{1}H nmr spectra of TTNZnCl$_2$ and TTNZnBr$_2$ at field strength of 100 Mc and sweep width of 500 cps.

Furthermore, depending upon the extent of delocalization of the nitrogen lone-pair electrons in the complexes, one might expect the appearance of the triplet pattern characteristic of the H–N coupling as found in quaternary ammonium salts.

In the TTNZnX$_2$ complexes, if it is assumed that the zinc atom has a coordination number of four and that in solution at room temperature the chemical environments of the two coordinated nitrogen atoms are equivalent, a seven- to nine-line spectrum, quite different from that of the free ligand, would be predicted. One absorption should arise from the $-C-CH_3$ protons and two absorptions should arise from the $-(CH_2)-$ and $-N-CH_3$ protons of the uncoordinated amine group. The chemical shift values of these three absorptions would be expected to agree closely with those found for the corresponding protons of the free ligand. The two amine groups that coordinate to the zinc atom form a six-membered chelate ring. This heteroatom ring can either take up a chair or boat conformation, as represented in Figure 5. In each conformation, the methylene carbon atom would bear protons in two different environments. The chair conformation gives rise to axial and equatorial protons, and the boat conformation gives rise to inner and outer protons. Since the ring contains two methylene carbon atoms in identical chemical environments, two absorption bands should appear due to the two types of methylene protons. In precisely the same way, each nitrogen atom would carry two different types of methyl groups, and thus two additional absorptions would arise. Again, owing to the coordination of the two nitrogen atoms, the latter four absorptions would be expected to suffer a downfield shift relative to the absorption positions of the corresponding protons belonging to the free amine group. Thus, a seven-line spectrum would be predicted. The integration ratios should show three sets of two equivalent protons, three sets of six equivalent protons, and one set of three equivalent protons.

If coupling between the two different types of methylene protons takes place, and if the coupling constant is sufficiently large, the two signals due to the different types of methylene protons should each split, giving the quartet pattern typical of an **AB** system. Thus a nine-line spectrum would be predicted. The possibility of observing a coupling between the two different types of N-methyl groups is very doubtful since, even in the case of the free ligand, fine structure due to coupling between the methylene and N-methyl protons was not resolved.

The ^{1}H nmr data for the complexes TSNZnX$_2$ (Table I) and TTNZnX$_2$ (Table II) clearly demonstrate that our preliminary structural assignments were correct. Firstly, the structural similarity of each LZnCl$_2$ with the corresponding LZnBr$_2$ complex is revealed by the fact that at each field strength the spectra of the two complexes are almost identical. Secondly, since the predicted qualitative spectra are in fact realized, the complexes TSNZnX$_2$ and TTNZnX$_2$ definitely have coordination numbers of five and four, respectively.

It is noted that in the TSNZnX$_2$ complexes the 60-Mc instrument did not detect the $-N-H$ signal. However, the 100-Mc spectra (Figure 6) clearly show the expected triplet bands, and in each case J_{H-N} has a value of 53 cps. This value, being identical with the value found for dimethylammonium chloride,[12] indicates that on coordination the delocalization of the nitrogen lone-pair electrons is appreciable. This is in agreement with the findings of the infrared spectral analysis and, as expected, is probably responsible for the observed downfield shift of the absorption bands in the TSNZnX$_2$ complexes relative to the corresponding positions of these bands for the free ligand. The fact that the absorption bands for both TSNZnCl$_2$ and TSNZnBr$_2$ have almost identical chemical shift values may indicate that in these five-coordinate systems the magnitudes of the downfield shifts are independent of the halide group. As predicted, the effect is largest for the -N–H proton.

In the TTNZnX$_2$ complexes the 60-Mc spectra presented some ambiguity which was resolved by the 100-Mc spectra (Figure 7). The latter spectra consist of nine absorption bands and thus indicate that the two different types of methylene protons which belong to the six-membered chelate ring system are indeed cou-

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[12] J. D. Roberts, *J. Am. Chem. Soc.*, 78, 4495 (1956).

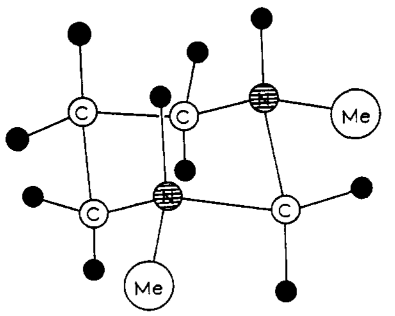

Figure 8. Structure of protonated N,N′-dimethylhexahydropyrimidine in the chair conformation: ● = hydrogen atom.

pled. These protons give rise to the AB quartet pattern composed of bands 1, 2, 5, and 6. The value of their coupling constant, 13 cps, corresponds favorably with the value of J_{11}, of about 12 cps, typical of geminal protons in the chair conformation of the cyclohexane system.[13] In the chair conformation the equatorial protons are deshielded and generally absorb at about 0.1–0.6 ppm lower field than axial protons.[14] In nitrogen heterocyclics, a much larger difference in chemical shift between the geminal protons adjacent to nitrogen has been noted. Δ(ae) of 0.92 ppm in the nmr spectrum of quinolizidine[15] has been associated with the effect of the axial lone-pair electrons on nitrogen which shield the axial protons in the adjacent methylene groups. Hamlow, *et al.*,[15a] postulated similar large differences in other nitrogen-containing heterocycles of frozen-ring conformation, in which the nitrogen lone pair is axial. Indeed, conformational analysis of several six-membered rings containing N-methyl groups at low temperatures have confirmed this postulate. The *sym*-hexahydrotriazines examined by Riddell and Lehn[16] show Δ differences for the ring protons of about 1 ppm. Lambert and Keske[17] found a large geminal chemical shift difference of 0.94 ppm for N-methylpiperidine and a small or normal value of 0.44 ppm for piperidine itself. The differences were associated with an axial lone pair in the former compound and an equatorial lone pair in the latter compound. Subsequently, Lambert, *et al.*,[18] further demonstrated that protonation of the N-alkylpiperidines, in which the lone pair is axial, results in a large decrease of Δ(ae) by about one-half for the methylene protons α to the nitrogen atom. However, in the case of piperidine itself, Δ(ae) of the methylene protons α to the nitrogen atom remained essentially unchanged with protonation. The effect on Δ(ae) of the γ-methylene protons, though slightly lowered, was approximately the same for all protonated species. Riddell[19] found that Δ(ae) of the α protons in N,N′-dimethyl- and N,N′-diethylhexahydropyrimidine was 0.96 and 1.06 ppm, respectively. On protonation of the above systems, we would expect Δ(ae) to decrease to about one-half of its original value by analogy to the findings of Lambert, *et al.* Comparison of the chair conformation of protonated N,N′-dimethylhexahydropyrimidine, Figure 8, with the similar conformation of our six-membered chelate ring system, Figure 5, reveals striking general similarities. Essentially, the structures would be identical except that the C_2 methylene group of the hexahydropyrimidine has been replaced by ZnX_2 and the C_5 methylene group has been disubstituted by $-CH_3$ and $-CH_2N(CH_3)_2$. Most significant and interesting are the respective values of chemical shift difference obtained for the two types of methylene protons of the six-membered chelate ring for $TTNZnCl_2$ and $TTNZnBr_2$ of 0.54 and 0.64 ppm. These are indeed about one-half the value of that found for the unprotonated hexahydropyrimidines. On the basis of this evidence, the six-membered chelate ring system is considered to be in the chair conformation, and the downfield doublet (bands 1 and 2) of the AB quartet pattern is assigned to the equatorial methylene protons, whereas the upfield doublet (bands 5 and 6) is assigned to the axial methylene protons.

Bands 3 and 4 are due to the orientationally different N-methyl groups of the chelate ring system. In contrast to the fairly large Δ(ae) of the methylene protons, the Δ(ae) of the N-methyl protons is much smaller, about 0.03 ppm for $TTNZnCl_2$ and increasing to about 0.06 ppm for $TTNZnBr_2$. These values agree quite well with recent nmr data[20] which show differences (0.03–0.16 ppm) between equatorial and axial N-methyl signals, the equatorial one lying at lower field. Thus bands 3 and 4 are assigned to the equatorial and axial N-methyl protons, respectively. The increase in Δ(ae) of the N-methyl protons and the methylene protons, which accompanies the substitution of Cl by Br, reflects a greater deshielding of the equatorial position relative to the axial position and may be attributed to the larger size of Br.

Bands 7 and 8 are due to the N-methyl and methylene protons, respectively, of the uncoordinated amine group. Band 9 is due to the C-methyl protons. The orientations of the uncoordinated amine group and the methyl group at the C_5 atom remain to be established.

Thus we conclude that in complexes of TSN with $ZnCl_2$ and $ZnBr_2$ the zinc atom has a coordination number of five due to the sterically unhindered tridentate behavior of TSN. The coordination geometry can be considered either in terms of a distorted trigonal bipyramid or a distorted tetragonal pyramid. The ligand TSN and the zinc atom give rise to a symmetrical cage-like structure made up of three six-membered rings (Figure 4). Each ring adopts the boat conformation. This generally labile system is maintained by the tridentate chelation of the ligand to the zinc atom. The strong tridentate behavior of

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(13) J. B. Stothers, "Techniques of Organic Chemistry," Vol. XI, Part I, Interscience Publishers, New York, N. Y., 1963, p 215.

(14) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 696.

(15) (a) H. P. Hamlow, S. Okuda, and N. Nakagawa, *Tetrahedron Letters*, 2553 (1964); (b) F. Bohlmann, D. Schumann, and H. Schulz, *ibid.*, 173 (1965); (c) F. Bohlmann, D. Schumann, and C. Arndt, *ibid.*, 2705 (1965).

(16) (a) F. G. Riddell and J. M. Lehn, *Chem. Commun.*, 375 (1966); (b) J. M. Lehn, B. J. Price, F. G. Riddell, and I. O. Sutherland, *J. Chem. Soc., B*, 387 (1967).

(17) J. B. Lambert and R. G. Keske, *J. Am. Chem. Soc.*, **88**, 621 (1966).

(18) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967).

(19) F. G. Riddell, *J. Chem. Soc., B*, 560 (1967).

(20) (a) J. E. Anderson and J. M. Lehn, *Bull. Soc. Chim. France*, 2402 (1966); (b) H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, **31**, 1073 (1966); (c) A. T. Bottini and M. K. O'Rell, *Tetrahedron Letters*, 423, 429 (1967); (d) A. T. Bottini, B. F. Dowden, and L. Sousa, *J. Am. Chem. Soc.*, **87**, 3249 (1965); (e) A. T. Bottini, B. F. Dowden, and R. L. van Etten, *ibid.*, **87**, 3250 (1965); (f) J. L. Imbach, A. R. Katritzky, and R. A. Kolinski, *J. Chem. Soc., B*, 556 (1966); (g) N. Mandava and G. Fodor, *Can. J. Chem.*, **46**, 2761 (1968).

TSN toward the ZnX_2 salts studied indicates that the ability of a tripod system to chelate is not determined by the presence of an apical functional atom. However, should there be an apical functional atom present, as in the cases of tren and its derivatives, it may find itself fortuitously close enough to the central metal atom, by virtue of ligand geometry, to become involved in coordination.

In complexes of TTN with $ZnCl_2$ and $ZnBr_2$ we conclude that the zinc atom has a coordination number of four due to the sterically controlled bidentate behavior of TTN. This restricted chelating ability of TTN is a manifestation of critical steric interactions that arise from neighboring N-methyl groups during complex formation. The coordination geometry of the zinc atom is most probably a slightly distorted tetrahedron. The bidentate coordination of TTN to the zinc atom gives rise to one six-membered chelate ring and an uncoordinated amine group (Figure 5). The chelate ring adopts a frozen pseudo-chair conformation at room temperature, the rigidity no doubt being due to the bulky substituents on the ring. The striking similarity between the ^1H nmr data of these systems and structurally analogous nitrogen-containing heterocycles indicates that the zinc(II) nucleus, though chemically different from the carbon atom, does not produce any conformational change in these systems. The fact that the ionic radius of zinc(II), 0.74 Å, is very similar to the covalent radius of carbon, 0.77 Å, probably accounts for the above results.

The postulated structures of the complexes can rationally account for all similarities and differences in physical data. Presently temperature-dependent ^1H nmr and three-dimensional X-ray studies are in progress in order to gain complete insight into the discrete molecular structures and properties of these complexes.

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Halomethyl–Metal Compounds. XXVI. Concerning the Mechanism of Dichlorocarbene Transfer from Trimethyltin Trichloroacetate to Olefins[1]

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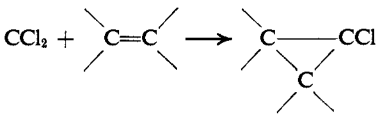
Abstract: An nmr investigation has shown that the CCl_2 transfer from trimethyltin trichloroacetate to olefins proceeds *via* intermediate trimethyl(trichloromethyl)tin and that the decarboxylation of the organotin ester is an autocatalytic process. The catalytic agent most probably is trimethyltin chloride. Conditions have been defined for the synthesis in high yield of 9,9-dichlorobicyclo[6.1.0]nonane by the reaction of trimethyltin trichloroacetate and cyclooctene in diglyme solution.

In a previous, brief study we investigated the possible utility of triorganotin trihaloacetates as CX_2 transfer agents.[4] It was found that trimethyltin and triphenyltin trichloroacetate did indeed decompose with carbon dioxide evolution on being heated at *ca.* 140°, and if such decomposition was carried out in the presence of an olefin, the expected *gem*-dichlorocyclopropane was formed. The product yields were only fair (40–55%), and no attempts were made to optimize this reaction for preparative purposes. A mechanism involving (trichloromethyl)tin intermediates was proposed (eq 1–3), but this suggestion was not

$$R_3SnO_2CCCl_3 \longrightarrow R_3SnCCl_3 + CO_2 \qquad (1)$$

$$R_3SnCCl_3 \rightleftharpoons R_3SnCl + CCl_2 \qquad (2)$$



(3)

backed up by experiment. It was known from other work in these laboratories[1,5] that trimethyl(trichloromethyl)tin serves as an effective CCl_2 transfer agent under exactly these conditions and that this transfer process most likely involves dichlorocarbene as an intermediate. However, this was not sufficient evidence and a clear demonstration was required that a triorgano(trichloromethyl)tin compound was indeed an intermediate rather than that the CCl_2 transfer from $R_3SnO_2CCCl_3$ to olefin was a concerted, one-step process. Nmr spectroscopy has served excellently to answer this question and to define the experimental conditions under which the $Me_3SnO_2CCCl_3$–olefin reaction is a high-yield process.

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(1) Part XXV: D. Seyferth and F. M. Armbrecht, Jr., *J. Am. Chem. Soc.*, 91, 2616 (1969).

(2) National Institutes of Health Predoctoral Fellow, 1964–1968.

(3) Postdoctoral Research Associate, 1968–1969.

(4) D. Seyferth, B. Prokai, and R. J. Cross, *J. Organometal. Chem.*, 13, 169 (1968).

(5) D. Seyferth, F. M. Armbrecht, Jr., B. Prokai, and R. J. Cross, *ibid.*, 6, 573 (1966).