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Review

METALLATRANES *

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Contents

* The authors dedicate this review to the outstanding Indian scientist Professor R.C. Mehrotra as a modest gift on the occasion of his 60th birthday. It is indeed a pleasure to acknowledge that R.C. Mehrotra has contributed a great deal to the chemistry of metallatranes in general and metal alkoxides in particular.

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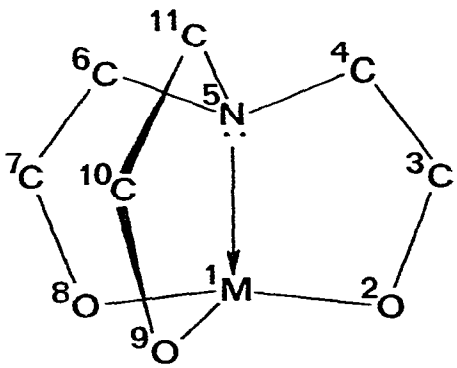
1. Introduction

Metallatranes, or simply atranes, are intramolecular complex cyclic esters or alkoxides of tris(2-hydroxyalkyl)amines having a metallatrane skeleton of general structure I,



I

where M is an *n*-valent element having inorganic or organic substituents when $n > 3$. The term metallatranes, proposed by one of the present authors in 1965 [1], is an abbreviation for the name of aminotrialkoxy derivatives of different elements which contain the above skeleton (I): so *a*mino*tr*ialkoxy*boranes* give "boratranes", *a*mino*tr*ialkoxy*silanes* – "silatranes", *a*mino*tr*ialkoxy*germanes* – "germatranes", *a*mino*tr*ialkoxy*phosph*o*ranes* – "phosphatranes", etc.

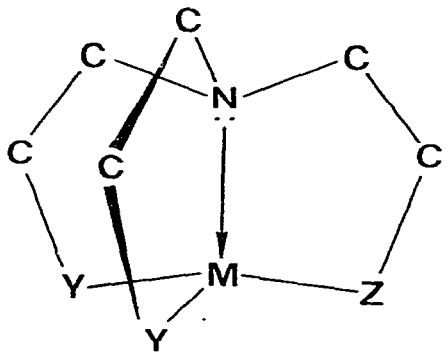
During the last two decades, metallatranes with M = B, Al, Si, Ge, Sn, Pb, P, Ti, V, Mo, etc. have been synthesized and studied. Of the reviews dealing with metallatranes, one [2] is out of date and the other [3] gives only a cursory consideration of these compounds as an example of metal alkoxides conversion.

The great and ever-increasing interest in these compounds is caused by not only the unusual nature of their cage structure and their physical and chemical properties but also by the specific biological activity of a number of these compounds. Some of them have been widely used or are coming into use in industry, medicine and agriculture. The formation of metallatranes and, especially, their

derivatives, metallatrane-3,7,10-triones, is widely used in the analytical practice.

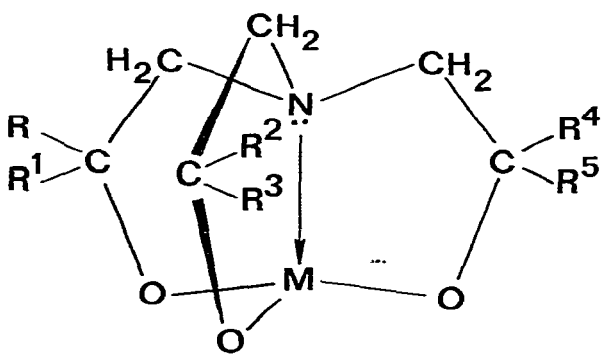
Boratranes and, especially, silatranes are the most comprehensively studied metallatranes. Silatranes are excluded from this survey, since they have been considered in a special monograph [4] and several reviews [5—9].

Apart from metallatranes, the present review deals with their analogs (II) which contain atoms of sulfur, nitrogen or carbon instead of one or three of the oxygen atoms. These include, in particular, 2,8,9-trithiametallatranes (IIa), 2,8,9-triazametallatranes (IIb), 2-carba- (IIc) and 2,8,9-tricarba-metallatranes (IId). Some attention is given to metallatrane derivatives, metallatran-3-ones



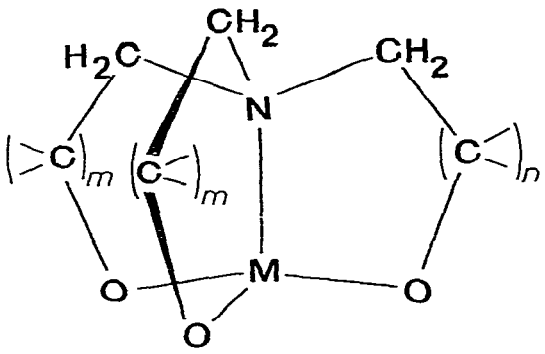
II (IIa Y = Z = S ;
IIb Y = Z = N ;
IIc Y = O , Z = C ,
IId Y = Z = C)

(IIIa) and 3,7,10-triones (IIIb) which are the corresponding derivatives of *N,N*-bis(2-hydroxyethyl)aminoacetic and aminotriacetic acids and, finally, to homo- and trihomo-metallatranes (IVa and IVb). These homo-derivatives may be regarded as the products of the insertion of one or three carbon atoms into the atrane skeleton (in the latter case, one into each O—C—C—N group). More simply, they are inorganic esters or alkoxides of bis(2-hydroxyalkyl)-(3-



III (IIIa . RR^1 = (O=), R^2 = R^3 = R^4 = R^5 = H ;
IIIb : RR^1 = R^2R^3 = R^4R^5 = (O=))

hydroxyalkyl)- or tris(3-hydroxyalkyl)-amines, respectively. This review covers the literature appearing until middle 1981.



IV (IVa $m = 1, n = 2$; IVb $m = n = 2$)

2. Metallatranes containing Group IIIA elements

2.1. Boratranes

Boratrane, the cyclic full ester of boric acid and triethanolamine (TEA), was first prepared in 1933 but patented as triethanolamine borate [10]. The cyclic structure, however, was proposed [11] for this compound only 15 years later. In 1951 Brown and Fletcher [12] proposed the existence of B ← N intramolecular coordination in boratranes. This seems to be the starting point for a systematic investigation of esters of boric acids with amino alcohols, having a "triptych" structure.

In the middle 1960's boratranes proved to be well-studied compounds and were considered in a number of reviews [13—15].

2.1.1. Methods of synthesis

The simplest synthetic route to boratranes is esterification of boric acid by tris(2-hydroxyalkyl)amines:

$$B(OH)_3 + (HOCHRCH_2)_3N \rightarrow \overbrace{B(OCHRCH_2)_3N} + 3H_2O \quad (1)$$

The reaction occurs both in solvents (water, chloroform [10], dimethylformamide [16], toluene [17], isoamyl alcohol [18], butanol/xylene mixture [19] and without solvents [12,20,21].

Boratranes are most readily prepared by transesterification of trialkylborates with tris(2-hydroxyalkyl)amines [22—26]:

$$B(OR')_3 + (HOCHRCH_2)_3N \rightarrow \overbrace{B(OCHRCH_2)_3N} + 3HOR' \quad (2)$$

The above reaction is most appropriate for the synthesis of boratranes having reactive substituents R, such as $ClCH_2$, H_2NCH_2 [22], and $HOCH_2$ [23]. The reaction proceeds upon short heating of the reagent mixture without any solvent [22—24] or in a medium of chloroform [24] or benzene [26].

The preparation of boratrane from boron anhydride and TEA is hindered by the formation of a difficult to remove and highly hygroscopic adduct of the boratrane with boric acid, $B(OCH_2CH_2)_3N \cdot H_3BO_3$ [25], which was later assigned a polymeric structure [22].

The aprotic method for the synthesis of boratranes is based on the reaction of trialkylborates with tris(2-acetoxyalkyl)amines in dry butanol in the presence of 9 mol% of sodium butoxide [16]:

$$B(OR')_3 + (CH_3COOCHRCH_2)_3N \rightarrow \overbrace{B(OCHRCH_2)_3N} + 3CH_3COOR' \quad (3)$$

The preparation of boratrane and its homo-derivatives by the reaction of tris-(diethylamino)borane with the corresponding trialkanolamines has been suggested [27].

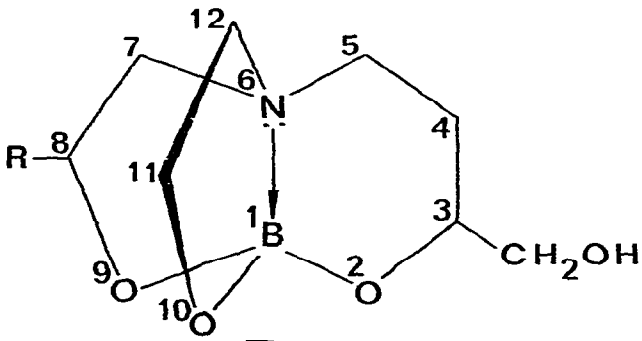
$$B[N(C_2H_5)_2]_3 + (HOCH_2CH_2CH_2)_mN(CH_2CHROH)_{3-m} \rightarrow$$

$$\overbrace{B(OCH_2CH_2CH_2)_m(OCHRCH_2)_{3-m}N} + 3HN(C_2H_5)_2 \quad (4)$$

V

R = H, m = 0 (a); R = H, m = 1 (b);
R = CH_3, m = 1 (c);
R = H, m = 2 (d); R = H, m = 3 (e)

Trihomoboratrane (Ve) [28] and 3,8-substituted homoboratranes (VI) were prepared by a reaction similar to eq. 2.



VI (R = $HOCH_2$, H_2NCH_2, CH_3, C_6H_5, $CH_2{=}CHCH_2OCH_2$, CH_3COOCH_2, $CH_3(CH_2)_{16}COOCH_2$, etc.)

The reaction of tris(diethylamino)borane with tris(2-mercaptoethyl)amine in benzene gave 2,8,9-trithiaboratrane (III) [29]:

$$B[N(C_2H_5)_2]_3 + (HSCH_2CH_2)_3N \rightarrow \overbrace{B(SCH_2CH_2)_3N} + 3HN(C_2H_5)_2 \quad (5)$$

Consecutive treatment of diethanolamine with formaldehyde, corresponding phenol and boric acid or trialkylborate afforded aromatic homoboratranes ring-fused in positions 3, 4 (VII) [30].

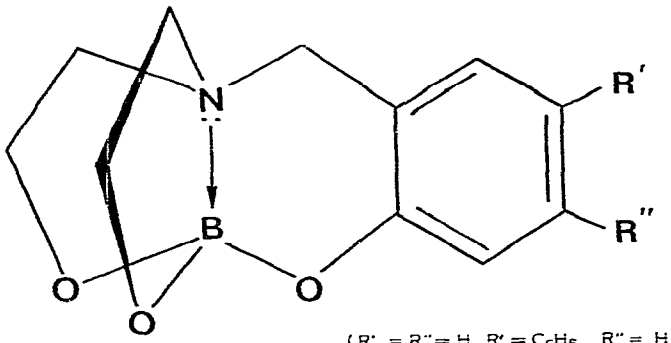
Boratrane-3,7,10-trione, a cyclic mixed anhydride of boric acid and aminotriacetic acid (ATA), was prepared by the interaction of the above acids [31,32]:

$$B(OH)_3 + (HOCOCH_2)_3N \rightarrow \overbrace{B(OCOCH_2)_3N} + 3H_2O \quad (6)$$

The reaction of ATA with trialkylborates proceeds even more readily [32]:

$$B(OR)_3 + (HOCOCH_2)_3N \rightarrow \overbrace{B(OCOCH_2)_3N} + 3HOR \quad (7)$$

Elemental boron may be used as the initial reagent in the reaction with ATA



VII (R' = R'' = H, R' = C_6H_5, R'' = H;
R' = p-$HOC_6H_3C(CH_3)_3$, R'' = H;
R' = HO_2C, R'' = H; R' = CH_3, R'' = OH;
R' = H, R'' = OH, R' = CH_3, R'' = H;
R' = $C(CH_3)_3$, R'' = H; R' = CH_3CONH, R'' = H)

[33]:

$$B + (HOCOCH_2)_3N \rightarrow \overbrace{B(OCOCH_2)_3N} + 1.5\ H_2 \qquad (8)$$

2,8,9-Tricarbaboratrane, 1-aza-5-boratricyclo[3,3,3,$0^{1,5}$]undecane, was obtained in 18% yield by hydroboration of triallylamine hydrochloride with (*N,N,N*-triethyl)borazane in petroleum ether [34]:

$$n(C_2H_5)_3N \cdot BH_3 + n(CH_2{=}CHCH_2)_3N \cdot HCl \xrightarrow{100-120^\circ C}$$

$$\overbrace{B(CH_2CH_2CH_2)_3N} + n(C_2H_5)_3N \cdot HCl + \left(N(CH_2)_3B\begin{matrix}(CH_2)_3N\\(CH_2)_3N\end{matrix}\right)_{n-1} \qquad (9)$$

2.1.2. Structure and physical properties

Boratrane and its 3-, 3,3'-diorgano derivatives are crystalline substances with a well-defined melting point (within the 48—264°C range) [10—12,16,22,25] *. However, 3,3',7-trimethyl- and 3,3',7,7'-tetramethyl-boratranes are wax-like subliming substances [22]. Among 3,7,10-substituted boratranes, only 3,7,10-trimethyl-, 3,7-dimethyl-, 10-vinyl-, 3,7-dimethyl,10-phenyl- and 3,7-dimethyl,10-piperidinyl-boratranes are crystalline compounds, all other being in the oily, waxy or glassy states [16,22]. The tendency of boratranes towards disordered aggregate states with an increase in number and size of substituents in the molecule is explained by the existence of a mixture of stereoisomers, distortion of the triptych structure and the polymeric state of the compound [22].

Boratrane is readily soluble in water, dimethylsulfoxide (DMSO), dimethylformamide (DMF) and is of limited solubility in acetonitrile and pyridine [12, 25]. Most boratrane derivatives are soluble in polar organic solvents and water

* Thus boratrane (m.p. 237—238°C) can be used for the identification of boron, if the B content of the material examined does not exceed 20% [35].

[10—12,16,22—27]. The solubility in non-polar solvents increases with ring expansion and an increase in the electron-withdrawing ability, size and number of substituents [16,22]. 3-Organo-substituted boratranes are even soluble in benzene, and 3,7,10-triorgano-substituted boratranes in alkanes.

Boratrane-3,7,10-trione is soluble in DMSO and DMF only upon heating [33]. 2,8,9-Tricarbaboratrane is readily soluble in organic solvents and is insoluble in water [34].

The structure of the boratrane and 3,7,10-trihomoboratrane molecules has been studied by X-ray diffraction [36—40]. The geometry of the boratrane molecule is shown in Fig. 1 [38].

The B ← N bond in these molecules is only 0.05—0.08 Å longer than the covalent B ← N bond in three-coordinate boron compounds [36—39]. In the boratrane molecule the boron and nitrogen bridge atoms form almost equally flattened tetrahedrons. Five-membered fragments display a β-envelope shape with a flat O—B—N—C fragment. The 3,7,10-trihomoboratrane trihydrate crystal, on the contrary, displays nearly tetrahedral N—B—O and B—N—C angles (108 and 110°, respectively), the six-membered rings being in the chair form [40]. The structural strain in the five-membered B—O—C—C—N rings in boratrane favors the B ← N bond formation. Despite the fact that the six-membered rings in trihomoboratrane are considerably more labile, the B ← N bond is of almost the same length (1.67 Å). The same B···N distance (1.666 Å) has been also found in the 2,8-dioxa-5-azaphenylborabicyclo [3,3,$0^{1,5}$] octane molecule [41]. In polar solvents, boratranes exist as monomers [12,25], and are associated in non-polar solvents [42,43]. A typical fragment consists of two or three molecules associated anti-parallel or successively ("head-to-tail" in both cases). In acetonitrile, boratrane is associated with quaternary ammonium salt ions [44].

The dipole moments [2,27,42—50] provide strong evidence for the existence of transannular B ← N coordination in the boratrane molecule. Thus, in dioxan, the dipole moment of boratrane is 8.0 [44] or 8.8 D [45,46], that of 3,7,10-trimethylboratrane is 6.51 D [47,48] (in benzene from 5.9 [2,49] to 6.7 D [50]).

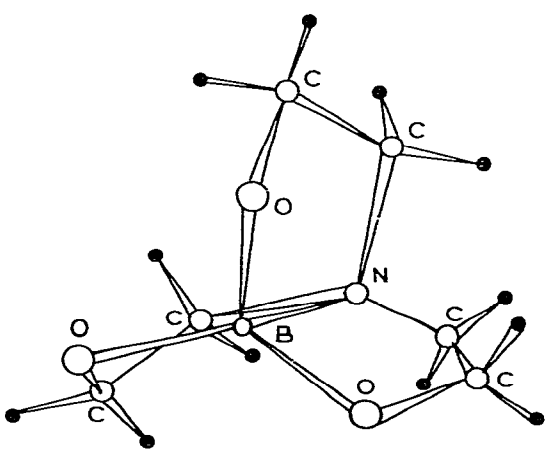
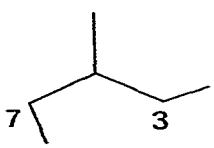


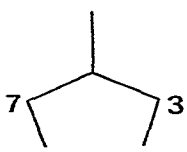
Fig. 1. Geometry of the boratrane molecule [38].

At the same time, the dipole moment of 3,7,10-trimethylboratrane calculated for the cage structure without B ← N bonding (with a planar boron configuration) is as low as 2.4 D [48]. The dipole moment of 3,7,10-trihomoboratrane (6.35 D in benzene) is 3.45 D higher than the value calculated without considering the B ← N [27].

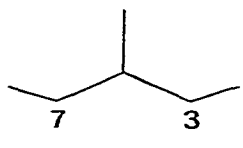
^{1}H [2,3,51—53], ^{11}B [54,55], and ^{15}N [56] NMR studies have contributed much to the understanding of the boratrane structure. The methylene proton resonance in the ^{1}H NMR spectra of boratrane is observed as two broadened $(AA'XX')_3$ triplets [51]. Degeneration indicates a high conformation mobility of the boratrane molecule in solutions. The presence of a substituent in position 3 freezes the conformation of the substituted five-membered atrane half-ring. The reason for such a rigid conformation has been revealed by an NMR examination of 3,7-di- and 3,7,10-tri-substituted boratranes [52]. The proton spectrum of 3,7-dimethylboratrane shows the molecules to exist in three diastereomeric forms in a ratio of 2 : 1 : 1.



VIII



IX



X

The equivalence of the 3,7-disubstituted rings in diastereomers IX and X is due to a fast (on an NMR time scale) ring conversion in the —80 to 200°C temperature range, which is an exchange process between two equally strained states of different shape where each CH_3 group occupies alternately equatorial and axial positions. This implies the conversion barrier of substituted rings in diastereoisomers IX and X to be extremely low and comparable to those of unsubstituted rings (less than 2 kcal/mol) [52]. This accounts for the fact that the molecular conformations of 3-methylboratrane and the two diastereoisomers of 3,7,10-trimethylboratrane are fixed.

A decreased coupling constant for the geminal interaction of protons of the 3-methyl-substituted atrane ring, $^{2}J_{AB}$, and the lower chemical shift, $\Delta\tau_{AB}$, in the metallatrane series show some flattening of the five-membered $\overset{\frown}{N—C—C—O—M}$ heterocycle, increasing with M in the following order [51]: O = V ≪ RSi < B.

The constant CH_2N proton shielding values in the ^{1}H NMR spectra of boratrane and its 3-, 3,7-di- and 3,7,10-tri-methyl derivatives as well as those of mono-, di- and tri-homoboratranes do not show any effect of the heterocycle substitution or of the extension to six-membered rings on the transannular B ← N bond strength [27,51,52]. Quite a different picture is observed when the oxygen atoms in boratrane are substituted by CH_2 groups: the NCH_2 protons in the ^{1}H NMR spectrum of 2,8,9-tricarbaboratrane are shielded similarly to the equivalent protons in TEA, their resonance being shifted more than 1 ppm upfield from boratrane [34]. This may be indicative of a considerably weaker B ← N interaction in the 2,8,9-tricarbaboratrane molecule despite the greater coordinating ability of the boron atom in trialkylboranes, in comparison with trialkylborates. The paramagnetic shift of the NCH_2 protons in the ^{1}H NMR spectrum of 2,8,9-

trithiaboratrane, $\overbrace{B(SCH_2CH_2)_3N}$ from tris(2-mercaptoethyl)amine (0.17 ppm) is lower as compared with boratrane (0.49 ppm relative to TEA), and this shows a weaker B ← N bond in the $\overbrace{B(SCH_2CH_2)_3N}$ molecule [29].

The ^{11}B nuclear resonance of boratrane is shifted upfields (—10.7 ppm) relative to trialkylborates [54]. The same effect is observed for tetrahedral boron in the $B(OH)_4^-$ anion and lithium tetramethyl borate, $LiB(OCH_3)_4$ (δ = —1.3 ppm and —2.9 ppm, respectively). This speaks in favour of a tetrahedral configuration of the boron atom and the presence of a B ← N bond in the boratrane molecule.

The ^{11}B NMR spectra of different boratrane and homoboratrane derivatives show an insignificant effect from the substituent nature on the ^{11}B nucleus shielding and a greater susceptibility of the ^{11}B resonance to the heterocycle size [55]. The ^{11}B deshielding consecutively increases from boratrane to 3,7,10-trihomoboratrane, $\overbrace{B(OCH_2CH_2CH_2)_3N}$. The ^{11}B chemical shift in the NMR spectrum of 2,8,9-tricarbaboratrane, $\overbrace{B(CH_2CH_2CH_2)_3N}$ is shifted to higher field by almost 5 ppm with respect to that of boratrane [34]. This most likely points out the effect of boron being attached to carbon atoms rather than the increasing extent of B ← N bonding in the 2,8,9-tricarbaboratrane molecule.

An attempt to define the effect of the B ← N bond on the ^{14}N resonance in the ^{14}N NMR spectrum of boratrane has not been a success due to low ^{14}N NMR sensitivity and a significant broadening of the spectral lines under the influence of quadrupole relaxation [57]. ^{15}N NMR spectroscopy has proved to be more valuable for defining the degree of the B ← N interaction in boratrane in a series of other metallatranes, $\overbrace{M(OCH_2CH_2)_3N}$, which increases with M varying in the following order [56]:

$$RGe \approx RSn < RSi < O = V < B \approx O_2Mo$$

The IR spectra of boratrane and its derivatives are at present sufficiently well examined [27,29,32—34,49,58—60]. The stretching of bonds in the boratrane skeleton is observed in the normal spectral region. The presence of a characteristic B ← N vibration frequency in the IR spectra might be an important feature of this bond in boratranes. This question, however, is not quite clear at present. There is even a body of opinion that the B ← N bond cannot be spectroscopically identified [46]. The frequencies within the range from 515 to 1270 cm^{-1} were assigned to the B ← N bond [2,3,32—34,58,49,59]. The bands at 1260 cm^{-1} [49] and 1271 cm^{-1} [34] were assigned to the B ← N bond in methyl-substituted boratranes and 2,8,9-tricarboboratranes, respectively. The band in the 510—548 cm^{-1} region was attributed to the B ← N bond of boratranes and boratrane-3,7,10-trione [27,29,32,33,59].
In the 500—1800 cm^{-1} region at 25°C and up to 50 kbar, the IR spectrum of boratrane is strongly distorted [60].

The photoelectron spectrum of boratrane shows a considerable negative charge on the boron atom due to bonding interaction of the vacant $2p$ orbital with a nitrogen electron lone-pair [61]. The electron lone-pair levels are closer than those in TEA.

In the mass spectra of boratranes the molecular ion peak intensity is low [62—64]. The initial electron-impact fragmentation of the boratrane molecule involves loss of a $C_nH_{2n+1}O$ fragment of the tricyclic system. In this case, the

most intense peak in the mass spectra of the boratrane [62,63] arises from the ion formed by elimination of a CH_3O unit and by an analogous cleavage of the substituted ring in the mass-spectra of methyl-substituted boratranes [63]. The $[M-OCHCF_2]^{+\cdot}$ ion peak is most intense upon fragmentation of C-trifluoromethyl-substituted boratranes [64]. Further fragmentation of the ions formed involves similar cleavage of the remaining rings [63].

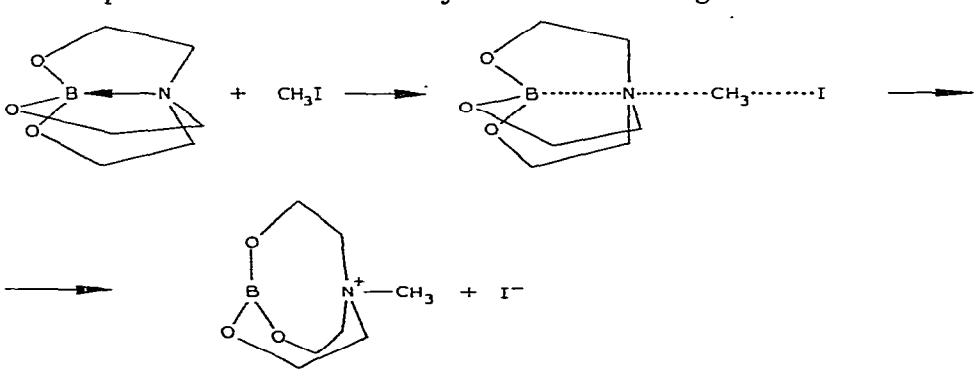
The thermophysical properties of boratrane might allow the B ← N bond dissociation energy and its contribution to the total energy of the molecule be determined. Measurements of the heat capacity and thermodynamic functions of boratrane have not revealed any anomalous behaviour within the temperature range from 4 to 350 K [65]. Above 250 K, however, the heat capacity increase gradient is enhanced. This is common for spherical molecules with high-temperature transitions [66]. The phase transition of boratrane occurs at 466.54 K [67]. The increment of the entropy (ΔS_t) and the enthalpy (ΔH_t) are 2.45 and 1.14 kcal/mol K, respectively, the entropy of melting of boratrane being equal to 11.26 kcal/mol K. The latter is almost twice as high as the limiting entropy for the plastic crystalline phase [66]. The temperature dependence of the dielectric constant of boratrane deviates only slightly from a monotonous curve at 474 K [68]. The deviation observed is too small to be attributed to the transition from the "triptych" structure having a B ← N bond ("*endo*-form") to the cage structure without the above bond ("*exo*-form"). The fact that the entropy transition is close to the Rln3 value (2.19 kcal/mol K) has suggested [67] a relationship between the transition and degeneration of the rotation about the N ← B axis in the crystal at temperature above the phase transition point.

The absolute value of the enthalpy of formation of boratrane in the gaseous phase proved to be 14.1 kcal/mol higher than that calculated taking account of the strain energy of each five-membered ring [69,70]. This difference is attributed to the B ← N bond energy.

2.1.3. Chemical properties

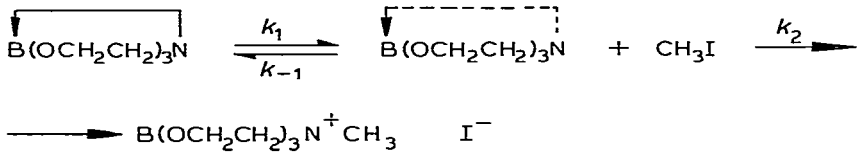
Attack of a reagent at the nitrogen or boron atoms of the boratrane molecule is hindered by steric factors, the rigidity of the structure and the existence of the B ← N transannular bond, causing higher coordination of the above atoms. However, the nitrogen atom is likely to display electron-donor properties [12,25,71,72].

Boratrane reacts with methyl iodide in acetonitrile 6×10^{-4} times as slow as TEA does [12]. The activation energy of this second order reaction is 18.5 kcal/mol for boratrane and 13.0 kcal/mol for TEA. The mechanism may involve electrophilic attack at the nearly tetrahedral nitrogen atom:



(10)

There may be an alternative mechanism involving breakage of the B ← N bond and which is consistent with kinetic data:



(11)

In $CHCl_3$, boratrane reacts with hydrogen chloride to form a hydrochloride, $B(OCH_2CH_2)_3N \cdot HCl \cdot 1/3\,CHCl_3$. With $HgCl_2$, $SbCl_3$ and $SnCl_4$ boratrane forms 4 : 5, 2 : 3 and 1 : 1 complexes, respectively [25]. In acetonitrile, boratrane reacts with $SbCl_5$ to give a complex, $B(OCH_2CH_2)_3N \cdot SbCl_5$ [71]. From the IR data the latter is a monomer with a trigonal-planar structure of the $B(O)_3$ group.

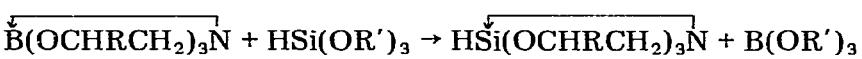
Boratrane reacts with chloramine in DMF to form a hydrazine derivative, $B(OCH_2CH_2)_3NNH_2^+Cl^-$ [72].

When treated with TEA methyl iodide, sodium tetramethylborate gives a bethaine-like boratrane adduct [73]:

$$NaB(OCH_3)_4 + (HOCH_2CH_2)_3N^+CH_3I^- \rightarrow$$

$$CH_3OB^-(OCH_2CH_2)_3N^+CH_3 + NaI + 3\,HOCH_3 \qquad (12)$$

Boratranes react with trialkoxysilanes in the presence of aluminium [74] or magnesium alkoxides to afford silatranes:



(13)

R = H, CH_3; R′ = CH_3, C_2H_5

A number of chemical transformations of various carbon-substituted boratrane derivatives have been studied [16]. 3-Vinylboratrane in chloroform at 0°C readily adds bromine to form 3-(1′,2′-dibromomethyl)boratrane in quantitative yield.

An attempt to reduce 3-(chloromethyl)boratrane with sodium hydride has led to a polymer of unidentified structure. 3-(Chloromethyl)boratrane does not react with sodium or magnesium methylate in boiling xylene, with potassium cyanide in DMF, copper cyanide in pyridine, or with sodium malonic ester or secondary amines in DMF, and fails to hydrogenate in the presence of palladium. The reaction of the above boratrane with methanolic sodium methoxide in a 1 : 1 ratio affords only traces of 3-(methoxymethyl)boratrane. With a 4-fold excess of sodium ethoxide, however, 3-(chloromethyl)boratrane in ethanol gave 3-(ethoxymethyl)boratrane in 65% yield. The reaction of 3-(chloromethyl)boratrane with potassium phthalimide in boiling DMF leads to 3-(phthalimidomethyl)boratrane, and with sodium acetate gives 3-(acetoxymethyl)boratrane.

3-(Aminomethyl)boratrane reacts smoothly with organic acid anhydrides. In the case of phenylisocyanate and phenylthioisocyanate, the above compound yields the corresponding phenyl- and phenylthiourea derivatives, and 3-(benzamidomethyl)boratrane in the case of benzoyl chloride.

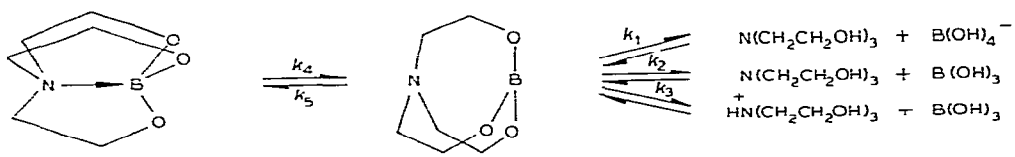
When heated to 240°C, boratrane decomposes to form solid (B_2O_3) and liquid (morpholine derivatives) and volatile (CO_2 and H_2O) products [71]. The poly-

condensation of an equimolar mixture of TEA with boric acid upon prolonged heating to 250°C [21] is likely to involve decomposition of the boratrane formed. The possible application of boratranes in the high temperature curing of epoxide resins is most likely to be due to the destruction rather than simple B ← N bond cleavage previously suggested [75].

Boratrane is cleaved by tetraphenylboronsodium in an aquous solution, whereas 3,7,10-trimethylboratrane is stable under the same conditions [76].

The neutral hydrolysis rate of boratrane and 3,7,10-trimethylboratrane is 130 and 535 $\times 10^5$ times, respectively, as slow as that of their acyclic analogs, triethylborate and triisopropylborate [82]. The hydrolysis of boratranes in both acid and base media is described by a first order kinetic equation and characterized by analogous activation parameters [46,77,78].

An aqueous solution of a mixture of TEA and boron acid contains up to 18—19% of boratrane [79,80]. Use of aprotic solvents shifts the equilibrium towards boratrane formation, whereas butanol causes no appreciable changes. Such a solvent effect suggests an equilibrium between two boratrane forms with planar and tetrahedral B configuration, the latter having a B ← N coordination bond. The formation of the above bond is presumed [80] to be a slow, (limiting) step following a rapid esterification process. From the kinetic data, a hydrolysis mechanism involving initial B ← N cleavage has been suggested [46,77]:



(14)

The hydrolysis of trisubstituted boratranes proceeds more slowly than that of boratrane [17,46,81,82], the hydrolysis rate being determined by the substituent nature [81]. The isokinetic $\Delta H = f(\Delta S)$ dependence reflects a more complex effect of the substituent in position 3 as compared with that of mono- and di-ethanolamine borinic and boronic esters [46,81]. The acid hydrolysis rate for 3,7,10-trimethylboratrane which is 4.11 $\times 10^5$ times as slow as that for boratrane is explained [82] by stabilization of the molecule due to shortening of the B ← N bond. According to the ^{11}B NMR chemical shifts of boratranes, however, this difference may be explained in terms of the molecular strain of the substituted boratrane molecule, which is expressed during the B ← N cleavage following the proton attack [55].

In going from boratrane to boratrane-3,7,10-trione, the hydrolysis stability of the molecule increases to a larger extent than in going to 3,7,10-trimethylboratrane [31—33]. Boratrane-3,7,10-trione is stable in boiling water and exhibits no changes upon heating to 240°C.

The B ← N transannular interaction stabilizes the 2,8,9-tricarbaboratrane molecule [34]. Unlike trialkylboranes, the above compound is stable to atmospheric oxygen and even to peroxides and reacts with neither ammonia nor triethylphosphine. This compound does not decompose much during water vapour distillation.

Boratranes do not react with diphenylcarbazone [83]. The boron determina-

tion is, therefore, carried out in these compounds by HCl treatment of a boratrane/sodium carbonate melt followed by alkaline titration [84].

2.1.4. Physiological activity

The low toxicity of most boratranes has allowed the possible application in neutron cancer therapy to be investigated [85—87]. Boratrane derivatives with amino acid fragments, providing a mechanism for borotrane transport into the cell have been considered most promising in this respect. However, the strong hygroscopicity as well as the appreciable toxicity (LD_{50} = 140 mg/kg for 3-(phthalimidoglutaminomethyl)boratrane) has prevented the use of boratranes of this type in therapy [85]. 3,7,10-Trimethylboratrane, which is capable for long retention in tumorous cells, has proved to be therapeutically most suitable.

Boratrane produces a sterilizing effect on Cochliomya hominivorax [88], a boratrane 3,7,10-trimethyl derivative being a stabilizer of amylolytic or proteolytic enzymes in sucrose on storage [89].

2.1.5. Possible applications

Boratranes are convenient synthons for the preparation of 1-hydrosilatranes [74]. These compounds have been suggested as catalysts for the esterification of aromatic dicarboxylic acids by alkene oxides [90], in the condensation of aminophenol with carboxylic acids for the synthesis of analgesics [91], as initiators of hydrodimerization of acrylonitrile to adipodinitrile [92] and the polymerization of polyisocyanates and their mixture with polyoles [93], as a cocatalyst of butadiene oligomerization in the purification of the butylene fraction from the pyrolysis and cracking of oil [94].

Boratranes efficiently accelerate the polycondensation reactions of epoxide resins with organic acids [95], phenols and alcohols [96] and may be used as curing agents for epoxide resins [17,30,72,75,97,98]. The TEA-triphenylborate complex, a potential source of boratrane, on the contrary, inhibits curing of thermosetting mixtures from diisocyanates, thus allowing these mixtures to be kept for more than 120 days [99]. Boratranes have been suggested as plastifiers [28,100] of, in particular, polyacrylonitrile [28] whose copolymer with vinylidene chloride is dyed better in the presence of boratrane [101].

The addition of boratranes to polyphenylene ethers increases their thermal- and light stability [102] and the addition to polyamides accelerates crystallization and minimizes adhesion to the mould [103].

Boratranes and boratrane betaine derivatives are components of corrosion inhibitors [73,104—107], pressure fluids [108,109], electrolytes suitable for work within the —55 to 125°C range [110], lubricants [105,111—113] and coolants for metal working [113,114]. The above compounds have been suggested as antistatic agents for polymers and wool [23,73,115] and as urea detectors [116].

2.2. Alumatranes

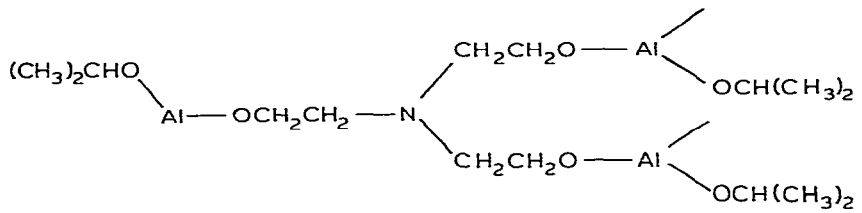
The atomic radius of aluminium, which is larger than that of boron (1.43 and 0.81 Å, respectively) accounts for appreciable differences in chemical and physical properties of alumatranes and boratranes.

2.2.1. Methods of synthesis and properties

The simplest alumatrane, $Al(OCH_2CH_2)_3N$, was prepared in high yield by the reaction of aluminium alkoxide with TEA in an aromatic solvent (benzene [117], toluene [118]) or with no solvent [119—122]:

$$Al(OR)_3 + (HOCH_2CH_2)_3N \rightarrow Al(OCH_2CH_2)_3N + 3HOR \quad (15)$$

3,7,10-trimethylalumatrane was synthesized in a similar manner (without any solvent [120,121] and in toluene [118]). The yield of alumatranes is highly dependent on the reagent ratio. Thus, one and a half excess of aluminium isopropoxide leads to a polymer [123]:



With a 3 : 1 ratio of the same reactants, a monomeric crystalline substance, $N[CH_2CH_2OAl(OC_3H_7\text{-}i)_2]_3$, is formed.

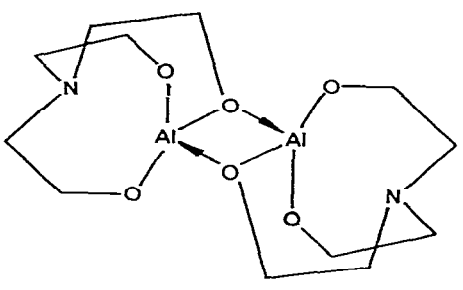
Transesterification of aluminium isopropoxide by tris(6-hydroxyhexyl)amine in toluene affords a cyclic ether [118]. TEA cleaves the Al—C bonds in triethylaluminium in toluene or hexane at —78°C to form alumatrane [124]:

$$Al(C_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow Al(OCH_2CH_2)_3N + 3C_2H_6 \quad (16)$$

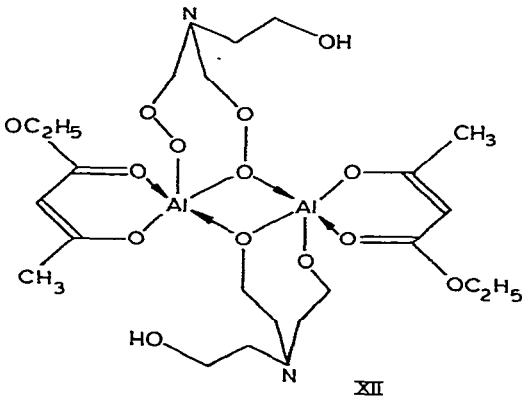
Alumatrane-3,7,10-trione, $Al(OCOCH_2)_3N$ is readily obtained as a dihydrate from the reaction of aluminium hydroxide with ATA in boiling water [33, 125—127].

Alumatrane is a white powder decomposing at 375—376°C [119]. It is readily soluble in chloroform, benzene, xylene, ethyl acetate, pyridine, nitromethane, is of limited solubility in acetone and dioxane, and is insoluble in ether. 3,7,10-Trimethylalumatrane sublimes without decomposition [118]. The melting point of this compound is about 182°C [120] or is within the 195—200°C range with partial melting at 80—100°C [118].

From cryoscopic and ebullioscopic data, alumatrane is associated in benzene to give octamers [119] or hexamers [117]. According to mass spectrometry data, alumatrane is a dimer [62] in the gaseous phase with the suggested structure XI:



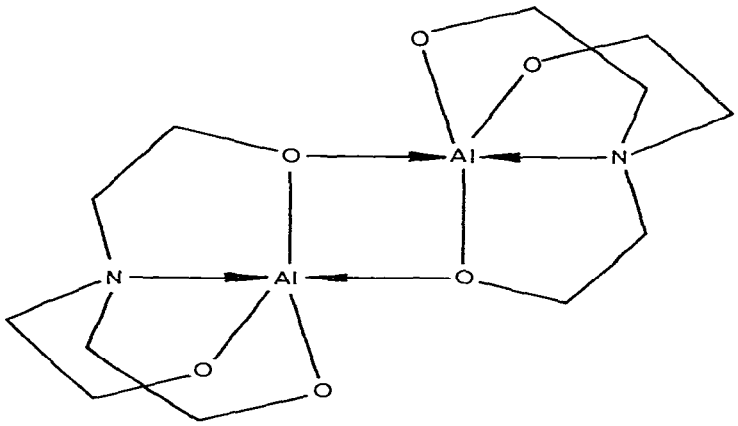
XI



XII

The above structure may be compared with that established by ^{1}H NMR spectroscopy for aluminium ethylacetoacetato-triethanolaluminate (XII) [128].

The dimer molecule (XII), however, contains pentacoordinate aluminium atoms of proposed trigonal-bipyramidal structure. It is not possible, therefore, to exclude the existence in dimeric alumatrane of a Al ← N interaction which may be reflected in the structure (XIII):



XIII

Alumatrane-3,7,10-trione dihydrate is a white crystalline substance soluble in water, DMF and DMSO, but insoluble in less polar solvents [33]. When heated in vacuum to constant weight or refluxed in decaline, the compound forms light brown, crystalline, anhydrous alumatrane-3,7,10-trione. The IR spectrum of alumatrane-3,7,10-trione and its hydrates displays intense $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ absorptions which indicate a significant ionicity of the Al—O bonds [59]. The Al ← N vibration in the alumatrane-3,7,10-trione molecule is observed in the 545 cm^{-1} region which is 20 cm^{-1} lower than that for the Al—N stretching vibration [129]. The ^{1}H NMR spectrum of alumatrane-3,7,10-trione in D_2O at pH $\leqslant$ 3 shows a narrow singlet indicating proton equivalence due to rapid conformational transitions averaging the position of the methylene protons relative to the carbonyl group [130,131]. The variations in the ^{1}H NMR spectra of less acidic solutions of the above compound (pH = 5—7) have been attributed [131] to ATA formed due to the hydrolysis. The ENN 1 *s* line energy in the X-ray photoelectron spectrum of alumatrane-3,7,10-trione is 1.1 eV higher than that in the spectrum of potassium aminotriacetate, $(KOCOCH_2)_3N$. This further indicates the Al ← N coordination [132].

Unlike that of boratrane, the maximum peak in the mass spectrum of alumatrane is that resulting from abstraction of the OCH_2CH_2 group from the molecular ion [62].

Alumatrane forms complexes through the nitrogen atom with hydrogen chloride, metal chlorides and diamminetetrarhodanochromium acid, as well as with picric, salicylic and other organic acids [119]. In contrast to boratrane, alumatrane forms adducts with dioxane and, possibly, with salicylic and *p*-aminobenzoic acids in which coordination occurs through the metal atom.

The reaction of tetrakis(2-oxyethyl)ammonium chloride with sodium tetra-

isopropoxyaluminate gives an alumatrane betaine derivative [73]:

$$^{-}Cl\,\overset{+}{N}(CH_2CH_2OH)_4 + Na^{+}\,Al(OC_3H_7\text{-}i)_4^{-} \rightarrow$$

$$HOCH_2CH_2\overset{+}{N}(CH_2CH_2O)_3\bar{A}lOC_3H_7\text{-}i + 3\,HOC_3H_7\text{-}i + NaCl \qquad (17)$$

Inorganic aluminium salt-TEA complexes [133] prepared by mixing equimolar quantities in methanol solutions, seem to have an analogous structure: $X_3Al\cdot N(CH_2CH_2O)_3AlX$ (X = NO_2, NO_3, NCS, Cl).

2.2.2. Applications

Alumatranes are efficient catalysts for the transesterification of dicarboxylic acid esters [118], cocatalysts for the removal of butadiene in the purification of the C_4-fraction from the cracking and pyrolysis of oil [24], and promotors for the formation of propyleneglycol in the oxo-synthesis [134]. Alumatranes are also used for the acceleration of thermoreactive resin curing and as stabilizers in the storage of cured resin [122]. They are the components of antiperspirants [120,135], and are introduced as a gelating agent in water-soluble dyers [121] and into glass-fibre adhesives [136]. Alumatrane betaine derivatives impart antistatic properties to fabrics and polymers [73].

The reaction of the acetylacetonate-TEA complex with tributoxy aluminium gives a product used as an ingredient in water-emulsion paints [137].

2.3. Metallatranes containing an atom of other Group IIIA elements

Gallium salt-TEA coordinate compounds have been prepared [138]. IR spectroscopic and elemental analysis data have allowed a structure to be assigned in which the gallium atom is chelated with the nitrogen atom of TEA, the inorganic anions being ligands: $Ga_2X_4(OCH_2CH_2)_2NCH_2CH_2OH$ (X = NO_2^{-}, NO_3^{-}, Cl^{-}).

However, the IR spectra of the above compounds, like those of the corresponding aluminium derivatives [133], may also indicate a structure of the following type:

$$XGa^{-}(OCH_2CH_2)_3N^{+}\cdot GaX_3$$

The reaction of tetrachlorotallium acid with TEA leads to a binuclear complex [139]:

$$2HTlCl_4 + 2(HOCH_2CH_2)_3N \rightarrow$$

$$Tl_2[(OC_2H_4)_3N][(OC_2H_4)_2NCH_2CH_2OH]Cl + 7HCl \qquad (18)$$

The facile Tl-TEA complex formation may be used for the determination of Tl^{I} and Tl^{III} ions at concentration not higher than 10^{-4} mol/l [140,141].

The Group IIIA element-ATA complexation has been studied in more detail [33,59,142—149]. At pH 3 this acid forms 1 : 1 and 1 : 2 complex salts with gallium [142—144]. The 1 : 1 salt was prepared with indium within the pH 2—10 range [143,145]. From potentiometric data, the coordination sphere of indatrane-3,7-10-trione may have up to three SCN^{-} ions [146].

The stability of Group IIIA metal-ATA complexes decreases in the following order [142]:

In > Ga, Al

Thallatrane-3,7,10-trione has been isolated as a monohydrate and as mixed complexes with sodium salts [126]. The monohydrate is sparingly soluble in water and retains the water of crystallization.

Thallatrane-3,7,10-trione dihydrate has been prepared from a hot aqueous solution of the salt and ATK, the analogous indium and thallium complexes being formed upon refluxing the hydroxides of these metals in aqueous ATA solution [33]. Upon heating in vacuum or refluxing in decaline gallatrane-3,7,10-trione dihydrate, only one molecule of water is lost. The dihydrate DTA data, however, show two endothermal maxima corresponding to consecutive loss of two water molecules. The ability of the Ga-ATA complex to form 1 : 1 chelates with oxalic [147], salicylic or sulfosalicylic [148] acids has been established by UV spectrophotometry. An ATA—oxalic acid exchange may occur to afford a complex ion, $Ga(C_2O_4)^-$ [147].

Bands in the 524—545 cm^{-1} region in the IR spectra of metallatrane-3,7,10-trione hydrates, $M(OCOCH_2)_3N$ (M = Ga, In, Tl) have been assigned to the M ← N stretching mode [59]. The difference in frequencies of symmetric and asymmetric vibrations, $\nu(COO^-)$, shows that the M—O bond is predominantly covalent for M = Tl, In and ionic for M = Ga. The presence of one $\nu_{as}(COO^-)$ band points to equivalence of the M atom bonds to all the carboxylic groups. This may indicate that the above metallatrane-3,7,10-triones are monomeric.

The ^1H NMR spectrum of thallatrane-3,7,10-trione reveals a ^{203}Tl— and ^{205}Tl—^1H spin-spin coupling evidently realized through the Tl ← N transannular bond [131].

3. Metallatranes containing a Group IIIB element

Refluxing praseodymium and neodymium triisopropoxides with TEA in benzene led to the formation of metallatranes, $M(OCH_2CH_2)_3N$ (M = Pr, Nd), according to the data from elemental analysis and IR spectroscopy [150]. Unlike the initial TEA, the IR spectra of the above compounds do not have the ν(OH) band in the 3360 cm^{-1} region, but do display three new bands in the 575—585, 545—550 and 280 cm^{-1} regions, attributed to the ν(M—O) absorption. The TEA-lanthanide derivatives do not melt up to 360°C, are insoluble and are possibly of polymeric nature.

The lanthanide-ATA complexation ability has been studied extensively [33,151—178]. Metallatrane-3,7,10-triones containing a lanthanide were prepared as crystalline hydrates from the reaction of lanthanide salts with sodium [151] or potassium [33,152] aminotriacetate as well as from the reaction of the corresponding oxide or salts [33,152—154] with ATA. In a basic medium, complexes of the type $HOM(OCOCH_2)_3N \cdot nH_2O$ form [155,156]. An increase in pH results in the following rearrangement of the complex formed at pH < 7 [157]:

$$La(OCOCH_2)_3N \cdot 3H_2O \underset{pH<7}{\overset{pH>7}{\rightleftharpoons}} H(HO)La(OCOCH_2)_3N \cdot 2H_2O \qquad (19)$$

The greater stability of the complex formed at pH > 7 is due to an enhanced ability of the ATA nitrogen atom to participate in the lanthanide coordinate bond.

Potentiometric titration of an equimolar mixture of lanthanide oxide (Ln^{3+}), ATA and hydroxyacids shows a step-wise addition of secondary ligand to the metallatrane-3,7,10-trione initially formed [158]. In this case, the constants for the formation of binary chelates are lower than that for metallatrane-3,7,10-trione and increase with an increase in the lanthanide atomic number.

The Ce^{III} $(OCOCH_2)_3N$ complex is oxidized to Ce^{IV} by atmospheric oxygen in alkaline solution [159—161].

The number and the bonding strength of water molecules in metallatrane-3,7,10-trione crystalline hydrates containing a lanthanide atom vary and depend on the nature of the lanthanide and the synthetic conditions. Complexes with lanthanides (Tb, Dy, Ho, Er, Yb, Y, Lu) contain four water of crystallization molecules and those with coordination number 6 (La, Pr, Nd, Sm, Eu, Gd) retain three water molecules, two of which are included into the inner sphere [162]. From the nuclear magnetic relaxation data, the coordination number of lanthanide complexes (Ce, Nd, Eu, Gd, Er) is 8 [163]. A decrease in the lanthanide ionic radius increases the distance between the metal atom and the ligand donating group.

A potentiometric study of the system Ln^{3+}-ATA-tyrone,-1,8-dioxynaphthalene-3,6-disulfoacid, or -pyrocatechine [164,165] (in a 1:1:1 ratio) has revealed the formation of triple chelates of the same composition, following an initial Ln^{3+}-ATA complexation. The stability of the mixed chelates increases in the following order: La < Pr < Nd. The difference in the stability of such complexes with ATA is used for the ion-exchange separation of heavy lanthanides [166].

Upon heating of yttrium subgroup lanthanide complex tetrahydrates, the first water molecule is eliminated at 40—110°C [152]. Crystalline hydrates, $\overset{\curvearrowright}{N}(CH_2COO)_3\overset{\curvearrowright}{La}\cdot 3H_2O$ and $\overset{\curvearrowright}{N}(CH_2COO)_3\overset{\curvearrowright}{Pr}\cdot 3H_2O$ lose two molecules at 100—160°C and the third one at only 225—300°C.

The IR spectra of crystalline hydrates and dehydrated metallatrane-3,7,10-triones do not depend much on the nature of the central atom [59,152,167—172]. In all the spectra, the C—N stretching is displaced by 22—23 cm^{-1} to longer wavelength relative to that in the IR spectrum of potassium aminotriacetate [167]. This may indicate the formation of a coordinate M ← N bond. The carboxyl group stretching frequencies in the spectra of lanthanide aminotriacetates and hydrates are similar to those of potassium aminotriacetate, thus pointing to an ionic character for the C(O)O—M bond [59,167—169]. The M—O bond in the metallatrane-3,7,10-triones considered seems to be weakened by the influence of the M ← N bond of the lanthanide as well as by the inductive effect of nitrogen [170]. The sharp difference in the IR spectra of lanthanide acetates and aminotriacetates is likely to be due to steric hindrance resulting from rigid bonding the ATA anion during the formation of the corresponding metallatrane-3,7,10-triones [171]. The steric factors are less important in La, Pr and Nd aminotriacetates where the metal has a larger radius [152].

In contrast to ν(C—N), the ν(C—H) bands are displaced to short wavelength [170], the greatest change accompanying the larger ν(C—N) band displacement to the longer wavelength region (metallatrane-3,7,10-triones with M = Al, Sc, Y, La). For anhydrous lanthanide aminotriacetates, however, the short-wavelength displacement of the C—H frequencies is smaller which seems to imply that

water is involved in the formation of a stable complex. This is well-defined for lanthanides of a larger radius (La, Pr, Nd). The IR spectra of anhydrous triacetates of the latter display a new band at 1380 cm^{-1}. The ν_s(C—O) bands are additionally split.

The ^1H NMR spectra of lanthanide aminotriacetates confirm the essentially ionic character of the M—O bonds [173].

The X-ray diffraction data have shown [152] the crystal lattice of lanthanide aminotriacetate pentahydrates to remain intact upon complete dehydration. Another picture is observed when one water molecule is removed from tetra- and tri-hydrates. The latter are able to lose water molecules even at low temperature. Complete dehydration of the complexes makes the latter amorphous.

Lanthanide aminotriacetate crystalline hydrates exhibit poor symmetry [174]. Depending on the lanthanide atomic number, the above compounds form several isostructural groups. Metallatrane-3,7,10-trione trihydrates containing an Sm, Eu or Gd atom crystallize as well-shaped pyramids.

The differences in properties of lanthanide-ATA complexes are used for the separation of mixtures of these compounds [175—178].

4. Group IVA metallatranes

4.1. Germatranes

4.1.1. Methods of synthesis

The reaction of trialkanolamines with germanium tetrachloride in a medium of chlorinated hydrocarbons and with ammonia as an HCl acceptor was carried out in 1962 [179]. The reaction, however, afforded only resinous products containing Ge—O—C bonds.

The first germatranes, 1-alkoxygermatranes, were obtained by Mehrotra in 1965 [180] by transesterification of an equimolar mixture of tetraalkoxygermanes with TEA in benzene:

$$Ge(OR)_4 + (HOCH_2CH_2)_3N \rightarrow RO\overline{Ge(OCH_2CH_2)_3N} + 3HOR \qquad (20)$$

$R = C_2H_5, (CH_3)_2CH$

The above reaction was further used by other authors [181].

1-Alkoxygermatranes readily undergo transesterification by alcohols to higher derivatives [180]:

$$R'OH + RO\overline{Ge(OCH_2CH_2)_3N} \rightarrow R'O\overline{Ge(OCH_2CH_2)_3N} + ROH \qquad (21)$$

$R = C_2H_5, (CH_3)_2CH$; $R' = C_4H_9, (CH_3)_2CHCH_2, (CH_3)_3C$

1-Organogermatranes were first prepared by cleavage of polyorganogermsesquioxides with TEA in xylene in the presence of potassium hydroxide [2,182—185]:

$$1/n(RGeO_{1.5})_n + (HOCH_2CH_2)_3N \rightarrow R\overline{Ge(OCH_2CH_2)_3N} + 1.5H_2O \qquad (22)$$

$R = CH_3, C_2H_5, \alpha$-$C_{10}H_7$ [182,183], adamanthyl [185]

Later, the transesterification of organotrialkoxygermanes, $RGe(OR')_3$, with TEA led to the corresponding carbofunctional germane derivatives, $R\overline{Ge(OCH_2CH_2)_3N}$ with R = ICH_2, $C_2H_5OCO(CH_2)_2$ [181], 2-SC_4H_3 [186], R''_3SiCH_2, $(R''O)_3SiCH_2$ [187].

An aprotic synthesis of 1-organo- and 1-halo-germatranes from the corresponding tetrahalogermanes or organotrichlorogermanes and tris(2-triethylstannoxyethyl)amine is based on reactions 23a and 23b [188—192]:

$$GeX_4 + [(C_2H_5)_3SnOCH_2CH_2]_3N \rightarrow X\overline{Ge(OCH_2CH_2)_3N} + 3(C_2H_5)_3SnX \quad (23a)$$

X = Cl, Br, I [188,189]

$$RGeCl_3 + [(C_2H_5)_3SnOCH_2CH_2]_3N \rightarrow R\overline{Ge(OCH_2CH_2)_3N} + 3(C_2H_5)_3SnCl \quad (23b)$$

R = CH_3, C_5H_5 [190,191], $CH_2{=}CH$, $CH{\equiv}C$, C_6H_5, $C_6H_5C{\equiv}C$, $C_6H_{13}C{\equiv}C$ [192]

Both reactions are carried out at —10 to 25°C. The yield of the corresponding 1-substituted germatranes is 60—98%.

1-Chlorogermatrane was obtained from the esterification of chlorotriethoxygermane with TEA [181]:

$$ClGe(OC_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow Cl\overline{Ge(OCH_2CH_2)_3N} + 3C_2H_5OH \quad (24)$$

1-Hydrogermatrane and its 3,7-dimethyl derivatives were synthesized in more than 50% yield from the reaction of triisopropoxygermane with tris(2-hydroxyalkyl)amine in benzene [193]:

$$(C_2H_5)_3N \cdot HGe(OR)_3 \cdot mHOR + [HOCH(CH_3)CH_2]_nN(CH_2CH_2OH)_{3-n} \rightarrow$$

$$HGe[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}N + (m+3)HOR + (C_2H_5)_3N \quad (25)$$

R = $CH(CH_3)_2$; m = 1—10, n = 0, 2

The reaction of tetramethoxygermane with TEA in a 3 : 4 ratio leads to tris 2-(1'-oxygermatranyl)ethyl amine [181]:

$$3Ge(OCH_3)_4 + 4(HOCH_2CH_2)_3N \rightarrow [\overline{N(CH_2CH_2O)_3Ge}OCH_2CH_2]_3N + 12HOCH_3 \quad (26)$$

The hydrolysis of the latter, as well as of 1-alkoxygermatranes, results in germatranol-1:

$$[N(CH_2CH_2O)_3GeOCH_2CH_2]_3N + 3H_2O \rightarrow$$

$$3\overline{N(CH_2CH_2O)_3Ge}OH + (HOCH_2CH_2)_3N \quad (27)$$

$$\overline{N(CH_2CH_2O)_3Ge}OR + H_2O \rightarrow \overline{N(CH_2CH_2O)_3Ge}OH + HOR \quad (28)$$

Alkyl(3-chloropropyl)diethoxygermanes react with diethanolamine in the presence of triethylamine in alcohol to form the corresponding 1-alkyl-2-carba-

germatranes [194]:

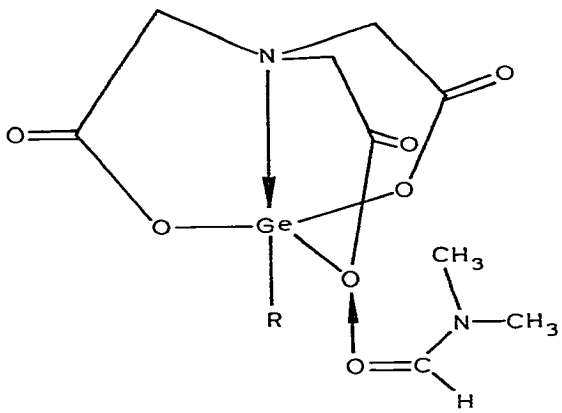
$$RGe(OC_2H_5)_2CH_2CH_2CH_2Cl + (HOCH_2CH_2)_2NH + (C_2H_5)_3N \rightarrow$$

$$RGe(OCH_2CH_2)_2N + 2HOC_2H_5 + (C_2H_5)_3N \cdot HCl \quad (29)$$

$$CH_2CH_2CH_2$$

R = CH_3 (yield is 22%), C_2H_5 (yield is 57%)

The reaction of *N,N*-bis(2-hydroxyethyl)aminoacetic acid with organotrialkoxygermanes leads to 1-organogermatran-3-ones, $RGe(OCH_2CH_2)_2(OCOCH_2)N$ (R = CH_3 and C_6H_5) [195]. A similar route with ATA gives 1-alkylgermatrane-3,7,10-triones, which are isolated as adducts with DMF (XIV):



XIV

$H_2Ge(OH)_6$ has been found [196] to form a 1:1 chelate with ATA.

4.1.2. Structure and physical properties

Most germatranes are colourless, crystalline substances with melting points usually higher than those of the isostructural silatranes [182]. 1-Hydrogermatrane melts with decomposition at 156—158°C whereas its 3,7-dimethyl derivative decomposes at 100°C without melting [193]. 1-Halogermatranes undergo decomposition at about 200°C [181,188].

These compounds are readily soluble only in water [181]. 1-Alkylgermatranes are soluble in highly polar organic solvents and alkyl halides [182]. 1-Arylgermatranes are only soluble in polar organic solvents. On a whole, the solubility of germatranes in non-polar solvents increases with a decrease in the Ge←N bond strength. 1-Alkyl-2-carbagermatranes are readily soluble in non-polar organic solvents [194]. 1-Organogermatrane-3-ones and 3,7,10-triones are of limited solubility in even highly polar solvents [195].

The crystallographic parameters of 1-organogermatranes reveal similar structures to the corresponding silatranes [182,197]. X-ray diffraction of Ge-substituted germatranes confirms the existence of the Ge ← N transannular donor-acceptor bond [194,195,198,200—204]. The bond length varies in a narrow

range from 2.2 Å in 1-iodomethylgermatrane to 2.3 Å in bis(1-germatranyl)-methane [198]. This value is only 0.3—0.4 Å higher than the sum of the Ge and N covalent radii (1.92 Å) and is considerably lower than the sum of the Van der Waals radii (3.8 Å) [199]. The coordination polyhedron around the germanium atom represents a distorted trigonal bipyramid (Fig. 2), the equatorial plane of which is formed by the oxygen atoms occupying the apexes of the equilateral triangle [200—202]. In 1-ethyl- and 1-(α-naphthyl)-germatrane molecules the germanium atom is displaced from the equatorial plane toward the substituent by 0.23 and 0.25 Å, respectively.

Similar to 1-organosilatranes [4], the five-membered heterocycles in 1-ethyl- [200,203] and 1-(α-naphthyl)-germatrane [201] molecules display an α-envelope conformation due to the displacement of the carbon atoms at the nitrogen atom from the ring plane [202]. The similar Ge ← N bond length in these molecules (2.24 Å) suggests that the nature of the substituent on the germanium atom does not affect the Ge ← N bond [201,202]. At the same time, a shortening of the Ge ← N bond length in the 1-(iodomethyl)germatrane molecule to 2.19 Å [198] indicates only a lower susceptibility of this bond to the nature of the substituent at the central atom, as compared to silatranes. This is also implied by the ^{1}H and ^{15}N NMR spectroscopic data [51,205,206]. The Ge···N distance in the 1-phenylgermatran-3-one molecule is 2.21 Å [195,198]. The Ge ← N bond in 1-methyl-2-carbagermatrane is much longer (2.44 Å [194,198]).

In the unit cell containing two molecules of bis(1-germatranyl)methane all four germatrane fragments have different geometries [198]. Thus, the Ge—C—Ge angles are 119.0 and 122.3°, and the Ge ← N bond varies from 2.26 to 2.32 Å. The considerably larger Ge···N distance in bis(1-germatranyl)methane seems to reflect the steric hindrance and mutal electrostatic effect of germatranyl groups separated by only one carbon atom.

In the ^{1}H NMR spectra of Ge-substituted germatranes the ring proton chemical shifts are close to those in the spectra of the corresponding silatranes [4,51, 205]. This indicates a similarity in the electronic structure of the silatrane and germatrane skeletons. The effect of the alkyl substituent R on the germanium atom in germatranes, $RGe(OCH_2CH_2)_3N$, on the chemical shifts of the CH_2-ring

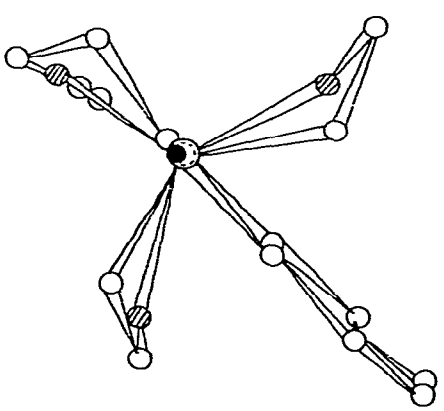


Fig. 2. Projection of the 1-(α-naphthyl)germatrane molecule [201]; ○ — carbon atoms, ⊘ — oxygen atoms, ○ — germanium atom, ● — nitrogen atom.

protons in the ^1H NMR spectra is transmitted via a δ-bond chain and through the Ge←N transannular bond [51,205]. The substituent R protons are less shielded in germatranes than in the corresponding silatranes. This may be caused by the decreased π-acceptor interaction of the germanium atom with the ring oxygen atoms than that of the silicon atom. The $Eu(fod)_3$-induced chemical shifts of 1-substituted germatranes are, in fact, larger than in the case of the corresponding silatranes [205]. This shows that the oxygen atoms in the germatrane skeleton are more electron-donating than those in silatranes.

Insertion of a methyl group into position 3 of the germatrane skeleton, as with other metallatranes, "freezes" the conformational transitions of the atrane rings, $GeOCH(CH_3)CH_2N$ [51]. The Ge—H proton resonance in the ^1H NMR spectrum of 3,7-dimethylgermatrane is shown by two singlets (5.79 and 5.85 ppm) with a 2:1 intensity ratio [193], although owing to the presence of two asymmetry sites, the existence of three diastereomers in a ratio of 2:1:1 might be expected by analogy with other 3,7-disubstituted metallatranes. This may be explained by a preferable formation of two less strained diastereomers of 1-hydro-3,7-dimethylgermatrane.

The ^1H NMR study of the metallotropic rearrangement in 1-cyclopentadienylgermatrane [190,191] has shown that the free energy $\Delta G^{\neq}_{300}$ of this process is larger than that of (trimethylgermyl)cyclopentadiene. This discrepancy has been attributed to a higher negative entropy value due to steric hindrance in the transition state, caused by the atrane system rigidity and by shielding of germanium by oxygen atoms. From the ^1H NMR data, the electron-donor effect of the germatranyl group, $Ge(OCH_2CH_2)_3N$, is lower than that of $Si(OCH_2CH_2)_3N$ and is close to that of $Ge(CH_3)_3$ [205].

The ^{15}N range in the ^{15}N NMR spectra of Ge-substituted germatranes, with solvents varying from CCl_4 to $(CH_3)_2SO$ is approximately 2.5 times smaller than that for isostructural silatranes [206]. This indicates a stronger Ge←N bond and a more rigid atrane skeleton as compared with analogous silatranes.

The higher coordination number of the germanium atoms in germatranes results in a stronger shielding of the Ge nucleus [207]. This is shown by an upfield shift of the ^{73}Ge resonance in the ^{73}Ge NMR spectra of 1-methoxygermatrane from tetramethoxygermane.

In the IR spectra of 1-substituted germatranes, the bands at 515—1135 cm^{-1} have been tentatively assigned to the Ge—O—C stretching and deformation vibrations of the alkyl groups [181]. The Ge←N bond absorption has been suggested to lie in the region below 300 cm^{-1}.

The 1-alkylgermatrane absorption bands in the UV spectra have a hypsochromic shift from the triethylamine bands. This displacement, however, is smaller than in the case of silatranes [208]. The blue displacement is assumed to characterize the extent of the Ge←N bonding. These data do not agree with the results of other investigations [200,205,206] indicating that the M←N transannular interaction is greater in germatranes than in silatranes.

The general route to electron-impact fragmentation of all germatranes, $XGe(OCH_2CH_2)_3N$, is abstraction of the substituent X from the germanium atom followed by elimination of CH_2O and CH_2 groups from the germatranyl ion formed, $[Ge(OCH_2CH_2)_3N]^+$ [192,209—211]. The intensity of the molecular ion peaks ranges from 6 to 44% of the base peak according to the ^{74}Ge

labelling. The germatrane skeleton ion is most intense when X = C_2H_5 and $C_6H_{13}C{\equiv}C$. In other Ge-substituted germatranes the intensity of the above ion decreases in the following order $CH_2{=}CH > Cl > C_6H_5 > C_6H_5C{\equiv}C > CH{\equiv}C$ [192]. The loss of the CH_2O fragments in the molecular ion of germatranes with X = C_6H_5, $CH_2{=}CH$ and $CH{\equiv}C$ gives ion peaks $M - CH_2O^+$ with intensities of 50% and more of the maximum. With X = Cl, the loss of the CH_2O unit gives rise to the base peak. The stability of the above ion depends on the σ^* Taft constant [212] of the substituent X. Fragmentation of such a type is also suggested [192] for germatranes having electron-acceptor substituents on the germanium atom (X = $C_6H_5C{\equiv}C$ and $C_6H_{13}C{\equiv}C$). This is confirmed by the presence of ion peaks formed by a consecutive loss of CH_2O units from M^+. The anomalously high relative intensities of peaks of ions having two metal atoms in the mass spectra of 1-(triphenylsiloxy)germatrane, 1-(1′-silatranylmethyl)germatrane and bis(1,1′-germatranyl)methane is explained by molecular ion rearrangement [211].

4.1.3. Chemical properties

1-Hydrogermatranes are hydrolytically and thermally unstable [193]. 1-Alkoxygermatranes react with water with retention of the atrane skeleton to form the corresponding germatranols according to eq. 28 [181]. This distinguishes the above compounds from 1-alkoxysilatranes of which the hydrolysis invariably involves the atrane ring cleavage [4].

The alkoxy group of 1-alkoxygermatrane is readily *trans*-esterified by alcohols [180] and triphenylsilanol [181]. 1-Methoxygermatrane reacts with acetic acid in the presence of acetic anhydride to form 1-acetoxygermatrane in nearly quantitative yield (98%) [181].

$$CH_3COOH + CH_3O\overbrace{Ge(OCH_2CH_2)_3N} \xrightarrow{(CH_3CO)_2O}$$

$$CH_3COO\overbrace{Ge(OCH_2CH_2)_3N} + CH_3OH \qquad (30)$$

Similarly to silatranol-1 [4], germatranol-1 reacts with trimethylchlorosilane in the presence of triethylamine to form 1-(trimethylsiloxy)germatrane [181]:

$$(CH_3)_3SiCl + HO\overbrace{Ge(OCH_2CH_2)_3N} + (C_2H_5)_3N \rightarrow$$

$$(CH_3)_3SiO\overbrace{Ge(OCH_2CH_2)_3N} + (C_2H_5)_3N \cdot HCl \qquad (31)$$

An analogous compound is formed when 1-chlorogermatrane is treated with triphenylsilanol.

Hexaalkyldimetallazanes are cleaved at the M—N bond by germatranol owing to the mobility of hydrogen in the hydroxy group:

$$[(CH_3)_3M]_2NH + 2HO\overbrace{Ge(OCH_2CH_2)_3N} \rightarrow$$

$$2(CH_3)_3MO\overbrace{Ge(OCH_2CH_2)_3N} + NH_3 \qquad (32)$$

M = Si, Ge, Sn

1-Ethylgermatrane reacts slowly with methyl iodide in acetonitrile to form the

quaternary salt, $C_2H_5Ge(OC_2H_4)_3NCH_3^+I^-$ [184]. Germatrane-3,7,10-triones form stable 1 : 1 complexes with DMF [195].

4.2. Stannatranes

4.2.1. Methods of synthesis

The reaction of organochlorostannanes, R_nSnCl_{4-n} with excess TEA leads to adducts of general formula $R_nSnCl_{4-n} \cdot mN(CH_2CH_2OH)_3$ (R = CH_3, C_4H_9, C_6H_5, CH_3O, C_2H_5O, $(CH_3)_3CO$; n = 1—3, m = 2) [213]. When the above reaction is carried out in an equimolar reagent ratio and in the presence of ammonia, water-soluble substances containing Sn—O—C groups are formed [179]. The product of the reaction of methyltrichlorostannane with TEA has a melting point of 260°C, which is close to that of 1-methylstannatrane (279°C) [209].

1-Organostannatranes are readily prepared in situ from organotrichlorostannanes and TEA sodium oxide in methanol [214,215].

$$RSnCl_3 + 3NaOCH_3 + (HOCH_2CH_2)_3N \rightarrow R\overset{\downarrow}{Sn}(OCH_2CH_2)_3\overset{\uparrow}{N} + 3NaCl + 3HOCH_3 \quad (33)$$

R = C_2H_5, C_4H_9, C_8H_{17}, C_6H_5 [214]; $(CH_3)_3SiCH_2$, $C_4H_9(CH_3)_2SiCH_2$, $C_6H_5(CH_3)_2SiCH_2$ [215]

Stannatranes can be prepared by cleavage of polyorganostannosesquioxides [216], polyorganostannonic acids [214,215,217,218], and polydiorganostannoxides [217,218] by TEA in aromatic solvents with [214,217,218] and without [215,216] potassium hydroxide:

$$1/n(RSnO_{1.5})_n + (HOCH_2CH_2)_3N \rightarrow R\overset{\downarrow}{Sn}(OCH_2CH_2)_3\overset{\uparrow}{N} + 1.5H_2O \quad (34)$$

$$1/n[RSn(O)OH]_n + (HOCH_2CH_2)_3N \rightarrow R\overset{\downarrow}{Sn}(OCH_2CH_2)_3\overset{\uparrow}{N} + 2H_2O \quad (35)$$

R = C_2H_5, C_4H_9 [214,217,218]; CH_3, C_6H_5 [217,218]; $(CH_3)_3SiCH_2$, $C_4H_9(CH_3)_2SiCH_2$, $C_6H_5(CH_3)_2SiCH_2$ [215]

$$1/n[R_2SnO]_n + (HOCH_2CH_2)_3N \rightarrow R\overset{\downarrow}{Sn}(OCH_2CH_2)_3\overset{\uparrow}{N} + RH + H_2O \quad (36)$$

R = CH_3, C_2H_5, C_4H_9, C_6H_5 [217,218]; $(CH_3)_3C$ [219]

Organotrialkoxy- and tetraalkoxy-stannanes undergo transesterification with TEA to form 1-organo- [209] and 1-alkoxystannatranes [220], respectively, in high yield:

$$RSn(OR')_3 + (HOCH_2CH_2)_3N \rightarrow R\overset{\downarrow}{Sn}(OCH_2CH_2)_3\overset{\uparrow}{N} + 3HOR' \quad (37)$$

R = CH_3, C_2H_5, C_4H_9, C_6H_5; R′ = C_2H_5 [209]
R = R′O; R′ = $(CH_3)_2CH$, $(CH_3)_3C$ [220]

1-Methoxystannatrane was prepared by alcoholysis of tetrakis(dimethylamino)stannane with TEA and methanol [221]:

$$Sn[N(CH_3)_2]_4 + (HOCH_2CH_2)_3N + CH_3OH \rightarrow$$

$$CH_3O\overset{\downarrow}{Sn}(OCH_2CH_2)_3\overset{\uparrow}{N} + 4HN(CH_3)_2 \quad (38)$$

The reaction of tetraacyloxystannanes with tris(2-triethylstannoxyethyl)-amine leads to acyloxystannatranes [189,222]:

$$Sn(OCOR)_4 + [(C_2H_5)_3SnOCH_2CH_2]_3N \rightarrow ROCOSn\overline{(OCH_2CH_2)_3N} + 3(C_2H_5)_3SnOCOR$$

$R = CH_3, C_2H_5, C_4H_9$ (39)

1-Organo-2,8,9-trithiastannatranes, $RSn\overline{(SCH_2CH_2)_3N}$, with R = CH_3, $(CH_3)_3C$ were obtained [223] from tris(2-mercaptoethyl)amine by a reaction analogous to eq. 36.

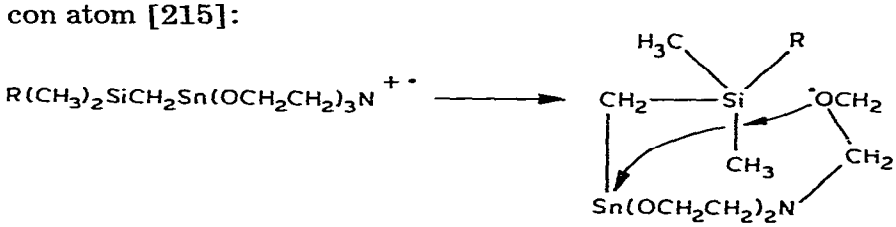
4.2.2. Structure and physical properties

1-Organostannatranes are colourless, microcrystalline or amorphous high-melting substances. They are relatively stable in water and soluble in polar solvents. The solubility of the above compounds decreases sharply on storage, possibly due to oligomerization, but may be increased by heating [215,216]. 1-Butylstannatrane is associated in benzene [216]; upon refluxing, the degree of association drops to 1.6. 1-Alkylstannatranes having no bulky Sn substituent are trimeric and dimeric in low-polar solvents and monomeric in water [223]. 1-t-Butyl- and 1-(*o*-tolyl)stannatranes are not associated in any solvent. 1-Alkyl-2,8,9-trithiastannatranes behave analogously.

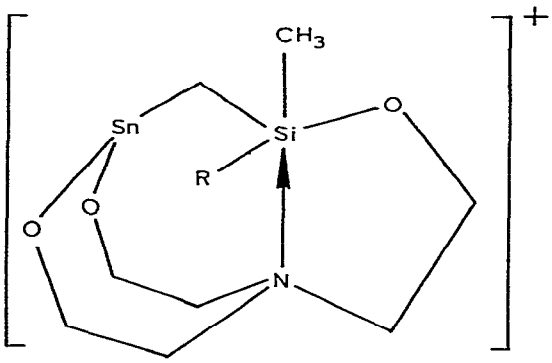
The dipole moments of stannatranes are 4.5—4.6 D which is in agreement with the value calculated for the pentacoordinate Sn state [218].

The IR spectra of 1-organostannatranes display normal bond stretching vibrations in the 4000—300 cm^{-1} region. The band at 484—495 cm^{-1} has been attributed to the Sn←N bond. The relative intensity of this band decreases with an increase in the solvent polarity. This is explained by interaction of stannatranes with the solvent, which displaces the equilibrium between the *exo* and *endo* forms [209].

In the mass spectra of 1-organostannatranes the intensity of the molecular ion is small [209]. Electron-impact fragmentation involves a consecutive loss of a CH_2O unit from each ring. Unlike the corresponding silatranes and germatranes, the ion peak of the stannatrane skeleton in the spectrum of 1-ethylstannatrane is rather weak. In the mass spectrum of 1-cyclopentadienylstannatrane, the predominant initial fragmentation involves cleavage of the Sn—C_5H_5 bond, as is observed with the corresponding germanyl derivative [210]. Similarly to 1-(triorganosilylmethyl)germatranes [211], the mass spectra of isostructural stannatranes display anomalously intense peaks of ions containing two metal atoms, which are formed by abstraction of one of the alkyl substituents from the silicon atom [215]:

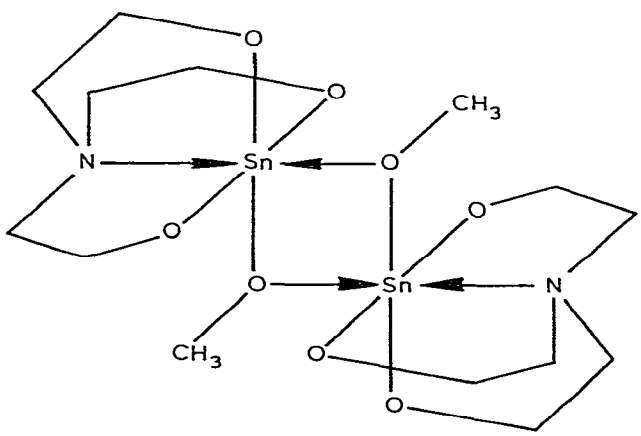


A molecular ion stabilization resulting from intramolecular rearrangement has been suggested:



XV

Studies of Mössbauer nuclear resonance (NGR) spectra of stannatranes have been carried out [214,217,221,224] to provide information on the tin coordination number in these compounds. The NGR spectrum of 1-methoxystannatrane displays a quadrupole splitting at 78 K (Δ = 0.54 mm/sec) [221]. The retention of the above splitting at room temperature as well at the isomeric shift region may indicate a hexacoordinate tin atom in the 1-methoxystannatrane molecule:



XVI

The quadrupole splitting observed in the NGR spectrum of 1-phenylstannatrane (1.18 mm/sec) is more different from that of alkylstannatranes (1.9—2.0 mm/sec) than might be expected from the substitution of the phenyl group by an alkyl group [214]. This seems to indicate a higher Sn coordination number due to the Sn←N transannular bond. Further analysis of the NGR spectrum, however fails to provide consistent data [217,224].

NMR spectroscopy is the most widely used technique for structural investiga-

tions of stannatranes [209,215,217,219,223,225]. Similarly to other metallatranes, the ^1H NMR spectra of 1-organostannatranes display the resonance of the OCH_2 and NCH_2 ring protons (0.3—0.4 ppm) down-field relative to TEA [209]. The temperature dependence of ^1H, ^{13}C and ^{119}Sn NMR spectra of 1-organostannatranes, $RSn(OCH_2CH_2)_3N$ with a small substituent R (CH_3, C_2H_5, C_4H_9, C_6H_5) sharply distinguishes these compounds from the metallatranes discussed previously. This dependence decreases with an increase in the substituent size and is not observed in 1-organostannatranes with R = $(CH_3)_3$ [219,223], *o*-$CH_3C_6H_4$ [223], $R'(CH_3)_2SiCH_2$ (R' = CH_3, C_4H_9, C_6H_5) [215] and in 1-organo-2,8,9-trithiastannatranes [223].

At room temperature, the ring OCH_2 and NCH_2 protons are exhibited as broad singlets and unresolved multiplets in the ^1H NMR spectra of 1-organostannatranes with R = CH_3, C_2H_5, C_4H_9, and C_6H_5, and the methyl group of 1-methylstannatrane as two broad lines of different intensity [209,219,225]. On increasing the temperature to 69—70°C (in $CHCl_3$) the signals become resolved: the OCH_2 and NCH_2 protons degenerate to triplets and the upfield methyl group signal (at 0.52 ppm) disappears. A decrease in temperature results in an additional splitting of the above upfield signal into equally intense peaks [219].

In the ^{13}C NMR spectra of the same stannatranes, the ring carbon atoms occur as broad, partly resolved temperature-dependent signals [219]. Of three ^{13}C methyl group signals in the spectrum of 1-methylstannatrane, the upfield ones are the first to coalesce with an increase in temperature.

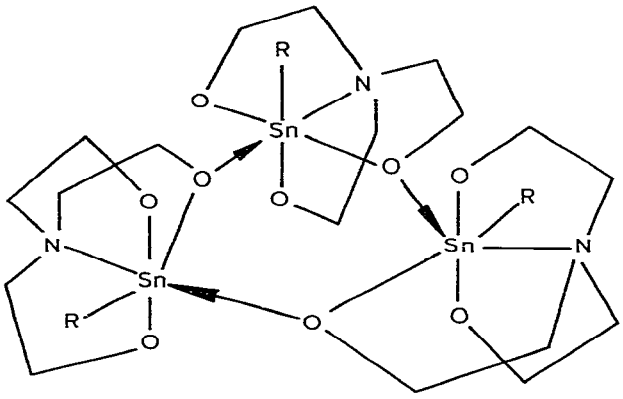
The ^{15}N NMR spectrum of 1-methylstannatrane-^{15}N displays two 2:1 signals invariable within the —30 to 33°C range.

At low temperature the ^{119}Sn NMR spectra of 1-alkylstannatranes display three equally intense signals. Two of these occur downfield and have very similar chemical shifts which coalesce at 25—50°C.

The temperature dependence of the NMR spectra of stannatranes was first explained [225] in terms of pseudorotation, i.e., slow conformational equilibrium between different configurations of the stannatrane skeleton, in which the nitrogen atom is in alternately axial (common to metallatranes) or equatorial position and ring inversion between chair-chair (cc) and boat-chair (bc) conformations at low temperature. Another explanation of the above phenomena is slow equilibrium interconversion between the *endo* and *exo* forms of the atrane skeleton of the stannatrane molecule and ring inversion of the former [209]. The upfield methyl proton signal (0.52 ppm relative to TMS, CCl_4, 29°C) in the ^1H NMR spectra of 1-methylstannatrane has been assigned to the *endo* structure having the cc conformation and the downfield signal (0.69 ppm, 29 to —20°C) to that having bc conformation. The increase in temperature accelerates the interconversion process, thus averaging the chemical shifts due to a rapid (on an NMR scale) exchange.

Another explanation of the temperature dependence of the NMR spectra of 1-organostannatranes containing sterically hindered Sn substituents involves association of molecules in organic solvents [219]. The associates are assumed to be of trimeric cyclic structure (XVII).

The increase in size of substituent R decreases the associate stability. This is exhibited in the ^1H, ^{13}C and ^{119}Sn spectra of 1-organostannatranes by a more



XVII

rapid signal coalescence with temperature increasing. The associates of 1-organostannatranes with bulky substituents R = $(CH_3)_3C$, *o*-$CH_3C_6H_4$, $R'(CH_3)_2SiCH_2$ form slowly, if at all [215,223]. The NMR spectra of the above compounds are resolved in the temperature range studied (—50 to 27°C).

The fact that the molecular weight of 1-organostannatranes varies depending on the solvent and the concentration [223] shows a more complicated behavior of the molecules in solution. In any event, this provides support for the formation of associates of various compositions.

4.2.3. Chemical properties

1-Organostannatranes react with CH_3I in acetonitrile 10—12 times as slow as does the initial TEA [209]. The fact that the nitrogen quaternization rate is considerably higher (200-fold) for stannatranes than for boratranes may be explained as due to either the steric effect of the relatively large tin atom, which flattens the nitrogen tetrahedron, or the equilibrium between the *endo* and *exo* forms of stannatrane molecules in solution. The rate constant for the above reaction decreases with increasing Sn-substituent size. The tendency of the molecules for association in solution decreases in the same order. One may propose, therefore, the existence of associated molecules with a structure more favourable to electrophilic attack at the nitrogen atom. It is not excluded, however, that the above process is preceded by nucleophilic attack at the tin atom by methyl iodide.

The ability of water molecules to disintegrate stannatrane associates [223], due to interaction of water oxygen with the hexa-coordinate tin atom, may be regarded as evidence supporting the above assumption.

4.3. Plumbatranes

The reaction of tetraethoxyplumbane with TEA gives $(C_2H_5O)_2Pb[OCH_2CH_2N(CH_2CH_2OH)_2]_2$, which has been suggested for use in pigment dispersion [226].

The reaction of lead tetraacetate with TEA is accompanied by reduction of Pb^{IV} to Pb^{II} and affords a 1:2 Pb^{II} acetate-TEA complex [227].

The reaction of PbO_2 with ATA in boiling water gave a compound which was assigned the structure of 1-hydroxyplumbatrane-3,7,10-trione dihydrate [153]. In the IR spectrum of the above compound, the difference between the $\nu_s(COO^-)$

and $\nu_{as}(COO^-)$ frequencies is as small as 180 cm^{-1}, indicating the predominantly ionic nature of the equivalent Pb—O(CO) bonds [59]. A large long-wave length shift (of more than 30 cm^{-1}) of the ν(C—N) band as compared with potassium ATA indicates the existence of strong Pb←N coordination.

5. Metallatranes containing a Group IVB element

5.1. Titatranes

5.1.1. Methods of synthesis

Water-soluble trialkanolamine esters of orthotitanic acid are prepared by the reaction of $TiCl_4$ with trialkanolamines in the presence of NH_3 as the HCl acceptor [179,228]. The reaction is carried out in an inert solvent [179] or in isopropanol [228]. Saturation of a chloroform $TiCl_4$ solution with ammonia followed by addition of isopropanol and an equimolar quantity of tris(2-hydroxyalkyl)-amine to the complex formed yields 1-isopropoxytitatrane or 1-isopropoxy-3,7,10-trimethyltitatrane [229]:

$$TiCl_4 + 4NH_3 + HOCH(CH_3)_2 + (HOCHRCH_2)_3N \rightarrow (CH_3)_2CHOT\overleftarrow{i(OCHRCH_2)_3N} + 4NH_4Cl \qquad (40)$$

R = H, CH_3

1-Alkoxytitatranes were synthesized by the reaction of equimolar amounts of tetraalkyltitanates with TEA [230—236]:

$$Ti(OR)_4 + (HOCH_2CH_2)_3N \rightarrow ROT\overleftarrow{i(OCH_2CH_2)_3N} + 3HOR \qquad (41)$$

R = C_2H_5, $(CH_3)_2CH$ and C_4H_9

A similar reaction of TEA with tetraalkyltitanates previously treated with stearic [237] or acrylic and metacrylic [238] acids gives the corresponding 1-acyloxytitatranes, $RCOOT\overleftarrow{i(OCH_2CH_2)_3N}$, with R = $CH_3(CH_2)_{16}$, or $CH_2{=}CHR'$ (R' = H and CH_3).

Co-transesterification of orthoalkyltitanates with equimolar amounts of tris(2-oxyalkyl)amine and phenol affords 1-aroxytitatranes [239]:

$$ROH + Ti(OR')_4 + (HOCCH_2)_3N \rightarrow ROT\overleftarrow{i(OCCH_2)_3N} + 4R'OH \qquad (42)$$

R = aryl, R' = C_2H_5, C_4H_9

The reaction of 1-isopropoxytitatrane with triorganosilanols and triorganostannane hydroxides leads to the corresponding triorganosiloxy- or stannoxytitatranes [230,231]. The same compounds can be prepared according to eq. 41 with $(R_3MO)_nTi(OC_3H_7\text{-}i)_{4-n}$ (M = Si, Sn) as the initial compounds.

Titanium(IV) tetrachloride reacts with ATA in DMF to form 1-chlorotitatrane-3,7,10-trione [153].

5.1.2. Physical properties and structure

1-Organoxytitatranes are, as a rule, crystalline substances having a fairly well-

defined melting point. The exceptions are the amorphous 1-isopropoxytitatrane and its 3,7,10-trimethyl derivative [229], 1-phenoxytitatrane and its *o*- and *m*-derivatives [239] and the wax-like 1-stearoxytitatrane [237]. 1-(Tributylstannoxy)titatrane is, under normal conditions, a liquid which can be distilled under high vacuum [230].

1-Organoxytitatranes are soluble in alcohols, DMF and nitrobenzene [229—232,234,238,239]; 1-alkoxytitatranes and (1,1′-dititatrane)oxide are fairly soluble in benzene. From ebullioscopic data, 1-alkoxy- [229] and 1-aroxytitatranes [239] are monomeric compounds. Cryoscopic data have shown, however, that 1-acroyloxytitatranes are associated upon dissolution in nitrobenzene. The associates consisting of 4—10 molecules, slowly disintegrate and 10—12 hours later have undergone complete or almost complete dissociation.

1-Aroxytitatranes display high dipole moments (about 8 D). This shows the existence of the Ti←N transannular donor-acceptor bond [239].

5.1.3. Chemical properties

Upon heating, 1-butoxytitatrane affords (1,1′-dititatrane)oxide [230]:

$$C_4H_9O\overleftarrow{Ti(OCH_2CH_2)_3N} \xrightarrow{\Delta} O[\overleftarrow{Ti(OCH_2CH_2)_3N}]_2 + (C_4H_9)_2O \qquad (43)$$

On standing, 1-(tributylstannoxy)titatrane gives hexabutyldistannoxane and a precipitate of a 1-(tributylstannoxy)titatrane-(1,1′-dititatrane)oxide complex:

$$3(C_4H_9)_3SnO\overleftarrow{Ti(OCH_2CH_2)_3N} \rightarrow$$

$$(C_4H_9)_3SnOSn(C_4H_9)_3 + (C_4H_9)_3SnO\overleftarrow{Ti(OCH_2CH_2)_3N}\cdot[\overleftarrow{N(CH_2CH_2O)_3Ti}]_2O \qquad (44)$$

1-Butoxytitatrane in benzene forms a 1 : 3 adduct with hydrogen chloride [234]:

$$C_4H_9O\overleftarrow{Ti(OCH_2CH_2)_3N} + 3HCl \rightarrow C_4H_9O\overset{\overset{HCl}{\vdots}}{Ti}(OCH_2CH_2)_3N\cdot HCl \qquad (45)$$
$$\underset{\underset{HCl}{\vdots}}{}$$

A similar 1-aroyloxytitatrane complex was obtained in nitrobenzene [238]. Hydrogen chloride in anhydrous ethanol, however, cleaves the 1-butoxytitatrane molecule to give TEA hydrochloride and a complex of dichlorodiethoxytitanium with an ethanol molecule [234]. The same products are formed by dissolution of 1-organoxytitatrane-HCl complexes in ethanol.

The reaction of 1-acroyloxytitatrane, $CH_2{=}CRCOO\overleftarrow{Ti(OCH_2CH_2)_3N}$ (R = H, CH_3), with HCl in dioxan leads immediately to an adduct of aroyloxytrichlorotitanium with dioxan and TEA hydrochloride [238]. Picric acid in benzene gives a 1 : 1 adduct with 1-acroyloxytitatrane (R = H); the latter decomposes in nitrobenzene. 1-(Methacroyloxy)titatrane (R = CH_3) reacts with the above acid in nitrobenzene to form a stable 1 : 1 complex. Analogously to HCl complexes, titatrane picrates are decomposed by alcohols.

1-Acroyloxytitatranes polymerize in the presence of azoisobutyric dinitrile or benzoyl peroxide to form coloured, transparent polymers soluble in lower alcohols. Copolymerization with methacrylate has afforded highly elastic copolymers.

5.1.4. Applications

The patent literature recommends titanium derivatives of tris(2-hydroxyalkyl)-amines for application in many different fields. These include use as catalysts for esterification [240] and transesterification [229], as well as for the preparation of *N,N*-diethyl-*m*-toluidine from *m*-toluic acid and diethylamine [241], diethylene glycol inhibitors in the preparation of polyethylene terephthalate [242], curing agents for epoxide resins [72,121,243—254], accelerators for silicone cross-linking [255,256] and polyformaldehyde stabilizers [257,258]. These compounds are also used to improve adhesion of anti-corrosion coatings [229,259—263] and insolubility of starch [264,265] and for water-proofing of paper and textiles [179,236,237,266—279]. Trialkanolaminotitatranes can be applied to the modification of polymers [235,280—287] and adhesives [136, 229,288], as dispergents [229,236,237,289,290], in moulding material [291], and for skin protection against UV-irradiation [292]. 1-(Triphenylstannoxy)-titatrane is a component of a fungicidal mixture [293].

5.2. Metallatranes containing other Group IVB elements

Zirconium derivatives of tris(2-hydroxyalkyl)amines are prepared, analogously to titanium derivatives, from the reaction of $ZrCl_4$ with TEA in the presence of ammonia as an HCl acceptor with [228] and without [179] addition of isopropanol to the reaction mixture. $ZrCl_4$ and TEA in a ratio of 1:2 in ethylacetate form a 1:4 complex [294]. From IR spectroscopy, the TEA molecule coordinate to the zirconium through nitrogen: $Zr[N(CH_2CH_2OH)_3]_4Cl_4$.

When heated to 180°C, a mixture of zirconic acid and TEA gives triethanolamine zirconate of 31.7% Zr content [287]. Tetraalkylzirconates react with TEA to form water-soluble compounds [236,296]. The same route has been suggested [236] for the synthesis of hafnium and thorium tris(2-hydroxyalkyl)-amino derivatives. These scarce data, however, do not allow the above compounds to be assigned the atrane structure.

The reaction of $ZrCl_4$ with ATA in aqueous solution has led to 1-chlorozirconatrane-3,7,10-trione trihydrate as a colourless, finely crystalline substance insoluble in either organic solvents or water [153]. A similar reaction of $ThCl_4$ with ATA affords a complex, $N(CH_2COO)_3Th \cdot N(CH_2COOH)_3 \cdot 3.5H_2O$, as a white, crystalline substance soluble in boiling water.

The IR spectrum of 1-chlorozirconatrane-3,7,10-trione trihydrate has a $\nu_{as}(C{=}O)$ band at 1740 cm^{-1} [59]. This, as well as a broad $\nu_s(COO^-)$ band, may indicate inequivalence of the three carboxy groups attached to Zr and the presence of a free carboxyl group.

Tetraalkylaminozirconates have been suggested for application as components in anti-corrosion mixtures [259,260,287] and as catalysts for the manufacturing of water-repellent compositions [179,270,278]. The above compounds are satisfactory for application as pigment dispergents and paper impregnating emulsions [236].

6. Metallatranes containing a Group VA element

6.1. Phosphatranes

6.1.1. Methods of preparation

The reaction of tris(dimethylamino)phosphine with TEA in large excess

(13 : 1) in a toluene-$CHCl_3$ mixture leads to the formation of the bicyclic ester in 15% yield [297—299]:

$$P[N(CH_3)_2]_3 + (HOCH_2CH_2)_3N \rightarrow P(OCH_2CH_2)_3N + 3HN(CH_3)_2 \quad (46)$$

It was not possible, however, to isolate the above compound [297].

The high basicity of phosphorus in phosph(III)atrane has allowed the following oxidation reactions to be carried out in solution resulting in a higher coordination number of the phosphorus atom * [297—299]:

$$4KO_2 + 6P(OCH_2CH_2)_3N \rightarrow 6O{=}P(OCH_2CH_2)_3N + 2K_2O \quad (47)$$

$$Y + P(OCH_2CH_2)_3N \rightarrow Y{=}P(OCH_2CH_2)_3N \quad (48)$$

Y = S, Se

$$H_3B{\cdot}O(CH_2)_4 + P(OCH_2CH_2)_3N \rightarrow H_3B{\cdot}P(OCH_2CH_2)_3N + O(CH_2)_4 \quad (49)$$

$$(OC)_5MX + P(OCH_2CH_2)_3N \rightarrow (OC)_5MP(OCH_2CH_2)_3N + X \quad (50)$$

M = Mo, X = CO; M = W, X = $NCCH_3$

Phosph(III)atrane reacts with trimethyloxonium tetrafluoroborane to form an adduct with HBF_4, $H\overset{+}{P}(OCH_2CH_2)_3\dot{N}^+\ BF_4^-$ [297]. The addition of triphenylmethyl tetrafluoroborate leads to $(C_6H_5)_3C\overset{+}{P}(OCH_2CH_2)_3\dot{N}^+\ BF_4^-$.

6.1.2. Properties and structure

P-substituted phosphatranes are crystalline, high-melting substances [297] soluble in polar organic solvents and insoluble in alkanes and ether. Similarly to the ^1H NMR spectra of other metallatranes [2,51], those of phosphatranes display OCH_2 and NCH_2 proton resonance shifted by 0.3—0.6 and 0.35—0.8 ppm downfield, respectively, compared to those of TEA [297]. Twice as large a diamagnetic shift is observed for the NCH_2 proton resonance of 1-H-phosphatrane and 1-(triphenylmethyl)phosphatrane tetrafluoroborates. The spectra of the above compounds and of 1-boranophosphatrane exhibit a coupling constant, ^3J(P—C) (12.8, 9.8 and 2.0 Hz, respectively). However, the ^4J(P—H) constant is not observed in the ^1H NMR spectrum of the latter compounds. This indicates the existence of an intramolecular P←N bond in the above phosphatrane fluoroborates. This is also confirmed by an upfield ^{31}P shift (20—53 ppm) in the NMR spectra of these compounds relative to their analogs, $RP(OCH_2)_3CCH_3^+$ and $RP(OCH_3)_3^+$ with R = H or $(C_6H_5)_3C$ [297,299]. The trigonal-bipyramidal configuration of the phosphorus atom in the 1-H-phosphatranyl cation is also evidenced from the ^1J(P—H) value in the ^{31}P NMR spectrum of the cation, which is 120 and 57 Hz lower than in $HP(OCH_2)_3CCH_3^+$ and $HP(OCH_2)_3^+$, respectively [297]. At the same time, the ^{31}P chemical shifts of 1-oxo-, 1-thio-, and 1-seleno-phosphatranes and 1-(pentacarbonyltungsten)- and 1-(pentacarbonylmolybdenum)-phosphatranes do not differ much from the corresponding analogs with tetracoordinate phosphorus, $YP(OCH_2)_3CCH_3$, where Y = O, S, Se, $(OC)_5W$ or $(OC)_5Mo$.

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* Use of other oxidants such as organic peroxides, trimethylamine *N*-oxide, $K_2S_2O_8$, N_2O_4 and singlet oxygen fails to produce 1-oxophosphatranes [297].

The methylene group chemical shifts in the ^1H NMR spectra of phosphatrane and TEA are very similar. The ^{31}P resonance in the NMR spectrum of phosph-(III)atrane is observed in the region characteristic of trialkylphosphites. This implies a pyramidal configuration of phosphorus in this bicyclic (2,2',2''-aminotriethyl)phosphite.

From X-ray diffraction data [298,300], the 1-thio- and 1-borano-phosphatrane molecules are of similar structure [297]. The configuration of phosphorus in these molecules is close to tetrahedral (the angle O—P—O is 106—110°), the geometry of nitrogen being almost trigonal-planar (C—N—C_{av} is 119.2 and 119.7°, respectively). The strained state of the molecules is shown by the N—C—C and C—C—O angles exceeding by 6—9° the tetrahedral angles. The P···N distance is 3.132 [297,298] and 3.098 Å [300] in thiophosphatrane and 1-boranophosphatrane, respectively, which is 0.3 Å smaller than the Van der Waals radii. Nevertheless, the above molecular geometry does not enable the presence of a P←N coordinate bond in these molecules to be assumed. From the NMR data, phosphatranes with Y = (O), (Se), $(OC)_5W$ and $(OC)_5Mo$ display an analogous structure [297].

The coordination polyhedron of the phosphorus atom in $[HP(OCH_2CH_2)_3N]^+$ represents an almost perfect trigonal bipyramid [297,298]. The interatomic P···N distance is 1.986 Å, i.e., 0.19 Å longer than the covalent P—N bond and approaching the P←N bond length in hexacoordinate phosphorus compounds [297]. The P—H bond in the above cation (1.35 Å) is 0.1 Å shorter than that observed in phosphines and PH^+ and is even smaller than the sum of covalent P and H radii (1.38 Å). The 1-(triphenylmethyl)phosphatrane cation seems to be of an analogous structure. A CNDO/2 calculation has shown that protonation of phosphorus in phosph(III)atrane and the *exo*-oxygen in 1-oxophosphatrane favours the formation of a transannular P←N bond [301]. The toxicity of phosphatranes is less dependent on the structure than in the case for silatranes [302].

The unusually high basicity of the phosphorus atom, due to the considerably strained state of the phosph(III)atrane molecule is responsible for the low stability of this compound [297,301] which is thermally unstable and readily polymerized on standing or concentration of the solution.

1-Oxo-, 1-thio- and 1-seleno-phosphatranes react with methyl iodide at 40°C in CH_3CN considerably more slowly (10 h) than TEA does (0.5 h) [297]. These compounds fail to react with trimethyloxonium tetrafluoroborates. Under the same conditions, however, 1-(pentacarbonyltungsten)- and 1-(pentacarbonylmolybdenum)-phosphatranes form the corresponding quaternary salts, $(OC)_5MP(OCH_2CH_2)_3NCH_3^+ \cdot BF_4^-$.

It is not possible to break the P—H bond in 1-H-phosphatrane tetrafluoroborate with $NaOCH_3$ [301]. 1-Boranophosphatrane do not enter exchange reactions with such bases as trimethylphosphite, triphenylphosphine, trimethylamine or pyridine [297].

6.2. Metallatranes having other Group VA elements

The reaction of tris(dimethylamino)arsine with TEA leads to a non-subliming polymer [303]. In analogy to phosph(III)atrane, the reaction may be expected to afford initially a readily polymerizable arsatrane, $As(OCH_2CH_2)_3N$.

Stibatrane has been prepared by the reaction of SbF_3 with 1-organosilatranes [304]:

$$SbF_3 + RSi(OCH_2CH_2)_3N \rightarrow Sb(OCH_2CH_2)_3N + RSiF_3 \qquad (51)$$

$R = CH_3$, $CH_2{=}CH$

Heating stibium oxides or chlorides with TEA to 50—250°C under low pressure affords stibium aminoalkoxides [305].

The reaction of bismuth hydroxide with TEA in the presence of sodium ethoxide in ethanol gives bismatrane, $Bi(OCH_2CH_2)_3N$ [306]. This compound is readily soluble in water and alcohol and less soluble in propylene glycol and methanol. In water bismatrane slowly hydrolyzes.

When refluxed in water, $SbCl_3$ and ATA form two complexes, $N(CH_2COO)_3Sb \cdot 4ATA$ [153,307] and $N(CH_2COO)_3Sb \cdot 3ATA \cdot H_2O$ [153]. Both complexes are soluble in water, DMF and DMSO only [153]. An intense absorption band at 1730 cm^{-1} in the IR spectrum of $N(CH_3COO)_3Sb \cdot 3ATA \cdot H_2O$ indicates the presence of free carbonyl groups.

Prolonged refluxing of an aqueous ATA solution with bismuth oxide gives a colourless finely crystalline powder, bismatrane-3,7,10-trione trihydrate, which is soluble in DMSO only. Bismatrane-3,7,10-trione dihydrate, $N(CH_2COO)_3Bi \cdot 2H_2O$ has been prepared in an analogous manner from bismuth carbonate and ATA [151]. When disoluted in hot water, bismuth oxide and a sodium aminotriacetic salt afford a water-soluble complex [308],

$$[\bar{O}COCH_2\overset{+}{N}H(CH_2COO)_2BiOH]_n \cdot [\bar{O}COCH_2\overset{+}{N}H(CH_2COONa)_2],\ n = 0\text{—}5.$$

The IR spectrum of bismatrane-3,7,10-trione trihydrate displays two $\nu_{as}(COO^-)$ bands at 1576 and 1554 cm^{-1} [159]. This shows either a polymeric structure of the compound or the presence of a H_2O-associated COOH group.

Stibium aminoalkoxides have been suggested as additives to polymers in order to enhance fire resistance [305] and to electrolytes for silver precipitation from cyanide solutions [309]. Complex stibium aminotriacetate inhibits the growth of Erlich ascites tumour [310], sarcoma 180 [311], the in vitro development of tumorous cells with leukemia and Brown-Perse tumour [312]. The above complex produces an antiblastic effect on SH-enzyme systems [313]. A water-soluble bismuth oxide-sodium triacetate complex has been proposed for treating syphilis [308,314]. Bismatrane catalyzes the formation of polymethyleneterephthalate [315].

7. Metallatranes containing a Group VB element

7.1. 1-Oxovanadatranes and 1-hydroxyvanadatrane-3,7,10-trionic acid

1-Oxovanadatranes have been prepared by the reaction of tris(2-hydroxyalkyl)amines with vanadium pentoxide, metavanadic acid and metavanadic ammonium salt or trialkylorthovanadates [2,3,316]:

$$V_2O_5 + 2[HOCH(CH_3)CH_2]_nN(CH_2CH_2OH)_{3-n} \rightarrow$$

$$2O{=}V[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}N + 3H_2O \qquad (52)$$

$$HVO_3 + [HOCH(CH_3)CH_2]_nN(CH_2CH_2OH)_{3-n} \rightarrow$$

$$O{=}\overset{\downarrow}{V}[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}\overset{\downarrow}{N} + 2H_2O \qquad (53)$$

$$NH_4VO_3 + [HOCH(CH_3)CH_2]_nN(CH_2CH_2OH)_{3-n} \rightarrow$$

$$O{=}\overset{\downarrow}{V}[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}\overset{\downarrow}{N} + 2H_2O + NH_3 \qquad (54)$$

$$O{=}V(OC_5H_{11})_3 + (HOCHRCH_2)_nN(CH_2CH_2OH)_{3-n} \rightarrow$$

$$O{=}\overset{\downarrow}{V}(OCHRCH_2)_n(OCH_2CH_2)_{3-n}\overset{\downarrow}{N} + 3HOC_5H_{11} \qquad (55)$$

$R = CH_3, ClCH_2$; $n = 0—3$

Reactions 52—54 were carried out by heating the reaction mixture in benzene followed by azeotropic distillation of water. The synthesis according to eq. 55 proceeds smoothly even at 20—23°C in chloroform.

Mixing the V_2O_5 or HVO_3-ATA water suspension until complete dissolution led to 1-hydroxyvanadatrane-3,7,10-trionic dihydrate [317] instead of the expected 1-oxovanadatrane-3,7,10-trione:

$$3V_2O_5 + (HOCOCH_2)_3N + 6H_2O \rightarrow$$

$$6[\bar{O}\overset{\downarrow}{V}(OCOCH_2)_3\overset{\downarrow}{N}]\overset{+}{H} + 2H_2O + 3CO_2 + 3CH_2O + NH_3 \qquad (56)$$

$$3H_2O + 6HVO_3 + 7(HOCOCH_2)_3N \rightarrow$$

$$6[\bar{O}\overset{\downarrow}{V}(OCOCH_2)_3\overset{\downarrow}{N}]\overset{+}{H}\cdot 2H_2O + 3CO_2 + NH_3 \qquad (57)$$

In the course of the above reactions (eq. 56,57), ATA reduces V_2O_5 to V_2O_4. 1-Hydroxyvanadatrane-3,7,10-trionic dihydrate is also formed upon refluxing aqueous suspensions of V_2O_4 and even V_2O_3. V_2O_3 is assumed to be first oxidized to V_2O_4 by atmospheric oxygen or ATA. It is not excluded, however, that the reduction of V_2O_5 and HVO_3 or the oxidation of V_2O_3 takes place during complexation with ATA and is due to the ready protonation of 1-oxovanadatrane-3,7,10-trione or oxidation of vanadatrane-3,7,10-trione, respectively, to the stable 1-hydroxyvanadatrane-3,7,10-trione. The reaction of triamylvanadate with ATA in DMF is also accompanied by oxidation to give 1-hydroxyvanadatrane-3,7,10-trione. An attempt to prepare 1-oxovanadatrane-3,7,10-trione by oxidation of 1-hydroxyvanadatrane-3,7,10-trione was unsuccessful. The formation of 1 : 1 V^{4+}-ATA complexes as well as the dependence of their structure on the pH of the aqueous medium have been investigated using spectrophotometry [318—320] and potentiometric titration [321].

1-Oxovanadatrane and its 3-mono-, 3,7-di- and 3,7,10-tri-substituted derivatives are colourless or greenish high-melting crystalline substances [316]. 1-Oxovanadatrane decomposes without melting at 260°C. These compounds are readily soluble in water. From cryoscopic data, 1-oxovanadatranes are monomeric in benzene and nitrobenzene. The dipole moment values (8.8—10.7 D) are almost twice as large as those calculated without consideration of

the V←N bond [322]. The ν(V=O) absorption bands (930—960 cm^{-1}) in the IR spectra of these compounds are strongly displaced to the low-frequency region as compared to O=VCl_3 (1035 cm^{-1}). In the ^1H NMR spectra of 1-oxovanadatrane and 3-methyl-1-oxovanadatrane, the internal chemical shift ($\Delta\delta$) between the OCH_2 and NCH_2 protons is approximately 0.5 ppm and is twice as small as that for silatranes, germatranes and boratranes [51].

The molecular ion peak in the mass spectra of 1-oxovanadatranes is weak (to 6% of the base peak intensity) [323]. The main route of the electron-impact fragmentation involves elimination of the OCH_2 species from the atrane rings. The selectivity of the dissociative ionization of C-methyl-substituted 1-oxovanadatranes is lower than that of the unsubstituted analogs.

1-Hydroxyvanadatrane-3,7,10-trione dihydrate is a blue, crystalline monomer, soluble in water, DMF, DMSO and alkylamines [317]. The presence of only two very intense absorption bands at 1575 cm^{-1} ($\nu_{as}(COO^-)$ hydrate) and 1630, 1650 cm^{-1}, respectively (ν_{as}(COOV)) in the IR spectra of 1-hydroxyvanadatrane-3,7,10-trione indicates the equivalence of the carboxyl groups attached to vanadium. The dihydrate water absorption is seen in the IR spectrum as a broad line at 3400—3500 cm^{-1} which is absent in the anhydrous compound.

The hyperfine structure of the EPR spectra of 1-hydroxyvanadatrane-3,7,10-trione has a mode common for $3d^1$ V^{IV} and is caused by interaction of the lone electron with the ^{51}V nucleus.

Aqueous 1-hydroxyvanadatrane-3,7,10-trione solutions are acidic (pK_a = 3.9). This accounts for the formation of sodium, potassium, barium [317], mercury, lead and ammonium salts [324]. In the monohydrate anion, $[OV(OCOCH_2)_3N \cdot H_2O]^-$ water ligands may exchange with SCN^- and N_3^- anions [324].

1-Oxovanadatrane enhances the activity of oxidoreductase enzymes of beans [325]. The bright colour of V^{5+}- or V^{4+}-ATA complexes is very helpful in the quantitative determination of this element [319,320].

7.2. Triethanolamine alkoxides of niobium and tantalum

Niobic and tantalic acids form hydrolyzable, polynuclear 5 : 2 complexes with TEA [326]. The quantitative determination of niobium by ATA titration in the presence of H_2O_2 has been described [327].

8. Metallatranes containing a Group VIB element

8.1. Chromatranes

The interaction of chromium compounds with tris(2-hydroxyalkyl)amines is at present little studied. In aqueous solution, $Cr(ClO_4)_3$ forms complexes with TEA [328,329]. At pH = 2.3—4.6, the Cr^{3+}-TEA mononuclear complex formation is faster than the hydrolysis [328]. The TEA-chromium salt has been proposed as an additive to polyolefins to improve colouring and light-stability [330]. The tris(2-methacryloxy)ethyl chromate-TEA salt has proved useful in anticorrosion mixtures [331].

Chromatrane-3,7,10-trione trihydrate, $N(CH_2COO)_3Cr \cdot 3H_2O$, is formed by the reaction of the chromium salt of a volatile acid with ATA in an aqueous medium [33,332] or by evaporation of the aqueous solution formed after

refluxing a $Cr(OH)_3$-ATA mixture in water [33]. Precipitation from such a solution by acetone or ethanol, however, gave chromatrane-3,7,10-trione dihydrate [151]. Under the same conditions, the addition of ammonium carbonate and precipitation by ethanol leads to ammonium complexes in which ATA is a tridentate ligand, $[(NH_4)_3]Cr[(OCOCH_2)_3N]_2 \cdot 4H_2O$, $[NH_4][(HO)Cr(OCOCH_2)_3N(H_2O)_2] \cdot 3H_2O$ and $NH_4[Cr(OH)(OCOCH_2)_3N(H_2O)] \cdot 2H_2O$ [333]. In these complexes, both the ATA ions and water ligands can exchange with such ligands as acetylacetone, *o*-phenanthroline, α,α-dipyridyl and oxalate anion [334] as well as with DMF and H_2O_2 [332].

At pH above 5.5, chromatrane-3,7,10-trione dihydrate deprotonates to give successively mono-, di- and tri-charged ions, $N(CH_2COO)_3Cr(H_2O)OH^-$, $N(CH_2COO)_3Cr(OH)_2^{2-}$ and $N(CH_2COO)_3Cr(OH)_3^{3-}$, respectively. This protolytic dissociation results in the substitution of the carboxyl groups by hydroxyls [336] and the association of the Cr^{III}-hydroxoacid complexes formed with bridging OH groups [336,337]. The 1:1 Cr^{3+}-ATA complex formation has been followed by potentiometry and photometry [338—340].

Chromatrane-3,7,10-trione trihydrate forms complexes with ammonia and amines and a potassium salt, $K[N(CH_2COO)_3CrOH \cdot H_2O]$ with KOH [332].

The IR spectra of chromatrane-3,7,10-trione trihydrate and its mixed complexes and salts show no absorption band arising from a free carboxyl group (1710—1730 cm^{-1}) [59,332]. The bands at 750—760 cm^{-1} and 750—760 cm^{-1} are assigned to Cr—O and water—ligand stretching, respectively. The water of crystallization OH group stretching is observed in the 3350—3490 cm^{-1} region.

8.2. 1,1-Dioxomolybdatranic and 1,1,3,7,10-pentaoxomolybdatranic acids

The synthetic routes to 1,1-dioxomolybdatranic acids, $[O_2Mo(OCRCH_2)_3N]^- H^+$, are based on the reactions of tris(2-hydroxyalkyl)amines with molybdenium anhydride, meta- or orthomolybdenic acid or ammonium molybdate according to the following schemes [2,5,341]:

$$O_nMo(OH)_{6-2n} + (HOCHRCH_2)_3N \rightarrow [O_2Mo(OCHRCH_2)_3N]^- H^+ + (3-n)H_2O \quad (58)$$

$$(NH_4)_2MoO_4 + (HOCHRCH_2)_3N \rightarrow [O_2Mo(OCHRCH_2)_3N]^- H^+ + 2H_2O + 2NH_3 \quad (59)$$

$R = H, CH_3$; $n = 1—3$

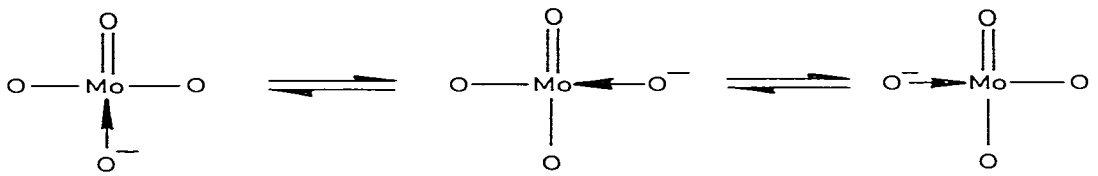
The above compounds are colourless, crystalline, high-melting, stable compounds, fairly soluble in water and of limited solubility in organic solvents.

1,1-Dioxomolybdatranic acid exhibits weak acidic properties, the pH value of a 0.1 *N* aqueous solution being 5.5 [342,343]. It was possible to prepare the salt of the above acid with piperidine, which is a colourless crystalline substance decomposing at ~280°C.

The 1-hydroxy-1-oxomolybdatrane structure suggested [341] previously for 1,1-dioxomolybdatranic acids failed to be confirmed by X-ray diffraction analysis [344]. The Mo atom in each of the two molecules of the unit cell represents a distorted octahedron with Mo←N bond lengths of 2.44 and 2.42 Å which are close to those of Mo-amine complexes. The existence of two shortened M—O bonds (1.75—1.83 Å) *trans* to the Mo—OC bond longer (2.34—2.35 Å)

compared to the other two bonds (1.91—1.97 Å) indicates the presence of two M=O double bonds. The lengthening of one of the Mo—OC bonds has been attributed to non-bonding repulsive intramolecular interaction. The *cis* structure of the dioxogroup of 1,1-dioxomolybdatranic acids is supported by the presence of a ν(Mo=O) doublet at 900—930 cm^{-1} in the IR spectra of these compounds [342,343].

The ^1H NMR spectrum of aqueous 1,1-dioxomolybdatranic acid solution shows equivalence of all three atrane rings [51,343]. This is explained [343] in terms of prototropic isomerization of the dissociated molecule where each of the Mo—OC bonds is alternatively coordinated, thus averaging the stereo-electronic structure of the rings:



In DMSO solution, the prototropic rearrangement of the molecule sharply slows down resulting in inequivalence of the protons of the NCH_2 and OCH_2 groups which are in different five-membered rings. Deceleration of this rearrangement is caused by strong solvation of the migrating proton. The rearrangement accelerates with increasing temperature or on dilution of the solution with water. These observations indicate the bound character of protons in 1,1-dioxomolybdatranic acid and explain the less acidic properties than might be expected for a delocalized-proton structure.

The application of TEA molybdate has been suggested for anti-corrosion protection of metals [345]. 1,1-Dioxomolybdatranic acid stimulates the nitrogen assimilating enzymes of beans [325].

The reaction of molybdenic acid with ATA in boiling water has afforded a 1:1 complex containing three water molecules [346]. The ^1H NMR spectrum of an aqueous solution of the complex with pH $\leqslant$ 5 shows a single peak of the N—CH_2 protons [346,347]. This implies a symmetrical structure for the complex molecule in water and an averaged environment of each methylene group, which does not make it possible to assign to the complex the 1-hydroxy-1-oxomolybdatrane-3,7,10-trione structure. The equivalence of the three Mo—$OCOCH_2$—N rings and the protons of each methylene groups is explained [346] by rapid dynamic transitions similar to those in 1,1-dioxomolybdatranic acid [343]. When the pH of a 1,1,3,7,10-pentaoxomolybdatranic acid solution increases above 5 the intensity of the proton signals decreases and a peak of ATA anion protons appears upfield [346,347]. This indicates cleavage of the Mo—O and Mo←N bonds with increasing pH [346].

The IR spectrum of crystalline 1,1,3,7,10-pentaoxomolybdatranic trihydrate exhibits two ν(OH) absorption bands at 3450 and 3528 cm^{-1} [346]. The peak at 1740 cm^{-1} is assigned to free carboxyl group absorption and provides support for the presence of such a group in the molecule.

Ammonium molybdate and ATA in boiling water form a colourless crystalline substance which was assigned a structure of a dihydrate ammonium salt

dimerized by an extra water molecule, $H_4N[\overset{+}{N}(CH_2COO)_3MoO_2]^- \cdot 2H_2O \cdots$ $H\text{-}O\text{-}H \cdots [O_2Mo(OCOCH_2)_3N]^+NH_4 \cdot 2H_2O$. Treatment of the above salt with excess boiling amine solution produces diammonium salts. A monosodium salt is formed by the reaction of ATA with equimolar quantities of NaOH and $(HO)_4MoO$. A disodium salt can be prepared from sodium molybdate and ATA. Mo^{VI} aminotriacetate or its ammonium salt give a white precipitate of $M[\overline{N}\text{-}(CH_2COO)_3\overline{Mo}O_2]_2$ (M = Pb, Hg) when treated with lead or mercury acetate in an aqueous medium.

The stability constants for the Mo^{VI}- and W^{VI}-ATA complexes have been determined by ^1H NMR spectroscopy and potentiometric titration. The difference in the hydrolysis rates may be used in quantitative determination of Mo and W in mixtures. The Mo^{VI}-ATA complex is diamagnetic. It occurs in aqueous solution as a dimer and is stable in the pH range 1—8 [348].

9. Metallatranes containing a Group VIII element

9.1. Ferratranes

Ferratrane was first prepared as a monohydrate by treatment of ammonium tetrachloroferrate and TEA hydrochloride in methanol or ethanol with ammonia [349]:

$$NH_4[FeCl_4] + (HOCH_2CH_2)_3N \cdot HCl + 4NH_3 + H_2O \rightarrow H_2O \cdot Fe(OCH_2CH_2)_3N + 5NH_4Cl \quad (60)$$

The same compounds are formed on heating dimethoxyferrate with TEA [350]:

$$Fe(OH)(OCH_3)_2 + (HOCH_2CH_2)_3N \rightarrow H_2O \cdot Fe(OCH_2CH_2)_3N + 2HOCH_3 \quad (61)$$

Hydrated water is removed by evaporation of a methanol-dioxan ferratrane monohydrate solution or by washing with dry ethanol [349].

Direct synthesis of anhydrous ferratrane is accomplished by the reaction of $FeCl_3$ with TEA hydrochloride in the presence of trimethylamine as an HCl acceptor [351,352]:

$$FeCl_3 + (HOCH_2CH_2)_3N \cdot HCl + 4(C_2H_5)_3N \rightarrow Fe(OCH_2CH_2)_3N + 4(C_2H_5)_3N \cdot HCl \quad (62)$$

Ferratrane and its *C*-methyl-substituted derivatives were obtained by transesterification of fresh $Fe(OH)_3$ with TEA in xylene [353]:

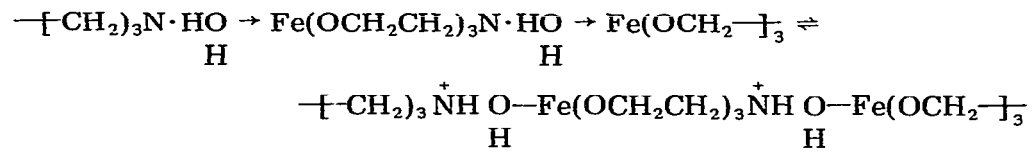
$$Fe(OH)_3 + [HOCH(CH_3)CH_2]_nN(CH_2CH_2OH)_{3-n} \rightarrow \overbrace{Fe[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}N} + 3H_2O \quad (63)$$

$n = 0—2$

Transesterification of $Fe(OC_2H_5)_3$ with TEA when mixing the reagents in benzene also leads to ferratrane.

Anhydrous ferratrane is an amorphous, readily hydrolyzable, grayish powder, insoluble in organic solvents [349,353]. Ferratrane monohydrate is a greenish-yellow, crystalline substance decomposing on heating [349]. Unlike the

anhydrous compound, it is readily soluble in alcohols, pyridine and $CHCl_3$. Ferratrane hydrate is assumed to be of oligomeric structure [349]:

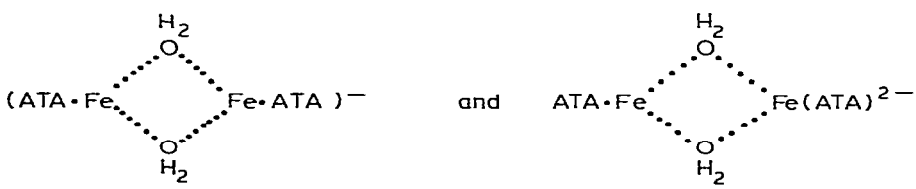


Dehydration of the above hydrate leads to polymerization. In a high-boiling oxygen-containing solvent (e.g. n-butanol), depolarization involving reduction of the chelate rings takes place.

Ferratrane-3,7,10-trione monohydrate was prepared by the reaction of metallic ferrum [354], ferric hydroxides or ferric ATA salts and ferric salts with ATA trisodium salt [33,355—361] in aqueous solution. Ferratrane-3,7,10-trione decomposes in aqueous ammonia and other basic media [356,361]. DMSO, DMF [361], H_2O_2 [361,362], 3-hydroxychinoline, tyrone, oxalic and chromotropic acids [363] substitute water ligands in Fe^{III} aminotriacetate. Ferratrane-3,7,10-trione is light-sensitive [360,364] and when exposed to light in aqueous solution decomposes to give CH_2O and CO_2. Ferratrane-3,7,10-trione monohydrate is stable to 185—190°C [360,361]. At 200°C in vacuum it dehydrates to an anhydrous compound [33,361].

The NGR spectrum of ferratrane-3,7,10-trione indicates an octahedral Fe configuration and predominantly ionic Fe—O(C) bonds [365]. At the same time, the presence of two lines in the NGR spectrum of ferratrane-3,7,10-trione hydrate may imply a polymeric structure [366]. The IR spectrum of this compound does not show absorption in the 1800—1700 cm^{-1} characteristic of free carboxyl group stretching [360,361]. An intense line at 900 cm^{-1} has been assigned [361] to coordinated water vibrations. Ferratrane-3,7,10-trione and its derivatives are paramagnetic [360,361,367].

Fe^{III}-ATA complexation has been studied by polarography [368—371] and paper chromatography [372]. The appearance of two bands on the ferratrane-3,7,10-trione potentiometric titration curve is explained by the presence of dihydrate dimers of the following type [360]:



as well as by the OH group insertion in the complex sphere and, with excess alkali, displacement of ligand water from the latter [373]. The 1:2 Fe^{III}-ATA complex has been assigned the following structure: $H_3Fe[(OCOCH_2)_3N]_2 \cdot 2H_2O$ [374].

The formation of ferric aminotriacetate is used for the analytical determination of Fe [375—838]. Ferratrane-3,7,10-trione has been suggested for absorption of nitrogen oxide [384]. This compound catalyzes diolefin polymerization [385] and may be used in chemical sources of electric energy [386], and as a

treatment against chlorosis of plants [354,357] and rancidity of seeds [387].

The metabolism of ferric aminotriacetate in the organism has been studied [388]. The stimulating effect of this compound on the synthesis of hemoglobin and hemoziderine as well as the ability to control the Fe level of plasma have been established [358,389,390].

9.2. Metallatranes containing a Co^{III} or Ni^{III} atom

The reaction of the corresponding tris(2-hydroxyalkyl)amines with Co(O)OH in xylene leads to cobatranes, $Co[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}N$ (n = 0—3) [353]. These are non-melting, readily hydrolyzable, violet-brown crystals soluble in methanol and chloroform. Cob(III)atrane-3,7,10-trione trihydrate is obtained by boiling freshly prepared aqueous $Co(OH)_3$ solution in ATA [153]. Dehydration of the above compound in vacuum at 160—220°C gives cob(III)-atrane-3,7,10-trione. Both compounds are readily soluble in water and DMSO. H_2O_2 treatment of a Co^{2+} sulfate-ATA mixture in an aqueous medium affords reddish-pink crystals of $H_6[Co(ATA)_3] \cdot 1.5H_2O$, readily soluble in water and decomposing at 130°C [151]. The reaction of $CoCl_2$, H_2O_2, $KHCO_3$ and ATA in water leads to potassium salts of Co^{III} aminotriacetate, with ATA as a tetradentate ligand [391]. The ^1H NMR spectra of these complexes in D_2O show the ionic character of the Co—O(CO) bond [392—393]. The ability of cobalt ions to form complexes with ATA has been suggested as a possibility for the removal of Co in technological processes [394], as well as in analysis [383,395,396]. Cobalt aminotriacetate protects seeds from rancidity [387].

Nickel(III)atrane-3,7,10-trione trihydrate has been synthesized analogously to the corresponding cobalt aminotriacetate [153] and isolated as green, water-soluble crystals. The IR spectrum of this compound indicates the predominantly ionic character of the Ni—O(CO) bonds [59].

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