

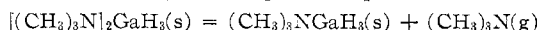
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Trimethylamine Adducts of Gallane and Trideuteriogallane

BY N. N. GREENWOOD, A. STORR, AND M. G. H. WALLBRIDGE

Received August 31, 1962

The new compounds $(\text{CH}_3)_3\text{NGaH}_3$, $(\text{CH}_3)_3\text{NGaD}_3$, $[(\text{CH}_3)_3\text{N}]_2\text{GaH}_3$, and $(\text{CH}_3)_2\text{SGaH}_3$ have been prepared. Trimethylamine gallane is a volatile solid, m.p. 70.5° ; a complete assignment of the gas-phase infrared spectra of this compound and its deuterio analog, m.p. 68.1° , indicate that the adducts are monomeric. At low temperatures the solid 2:1 adduct forms; this dissociates above about -63° (1 mm.) according to the equation



The dissociation pressure is 378 mm. at 0° and the heat and entropy of dissociation are 10.35 kcal./mole and 36.5 e.u. The dimethyl sulfide adduct is stable at -70° but decomposes at room temperature into gallium, hydrogen, and the ligand.

The addition compounds of gallane (GaH_3) occupy an important place in the coordination chemistry of trivalent gallium and of group III in general. The preferred stoichiometries of adducts of gallium trichloride, tribromide, and trimethyl are now well established and there is fragmentary information for the triiodide and triethyl.¹ Moreover, the relative stabilities and heats of formation of many of these adducts and their boron² and aluminum³ analogs have been determined and correlated. Corresponding information on the stoichiometry, structure, and stability of the coordination compounds of gallane is almost completely lacking despite the obvious interest which attaches to these adducts on two counts: first because they effect a link between the complexes formed by organogallium compounds on the one hand and the gallium trihalides on the other, and second because they extend the intricate sequence of hydride complexes formed by the boranes and alane (AlH_3).

Lithium gallium hydride, which can be regarded as the addition compound $\text{Li}^+[\text{H}^- \rightarrow \text{GaH}_3]$, is less stable than LiBH_4 or LiAlH_4 and is a milder reducing agent.⁴⁻⁶ It decomposes slowly at room temperature to give lithium hydride, gallium, and hydrogen. An adduct with diethyl ether has also been mentioned⁵ but was not characterized and has recently been discounted.⁷ It was therefore decided to investigate a series of amines as ligands since these are invariably stronger than ethers and might be expected to stabilize the fugitive gallane moiety more effectively. The present paper reports the use of lithium gallium hydride to prepare the relatively stable compound $(\text{CH}_3)_3\text{NGaH}_3$, which, in turn, was used to prepare the less stable adducts $[(\text{CH}_3)_3\text{N}]_2\text{GaH}_3$ and $(\text{CH}_3)_2\text{SGaH}_3$.

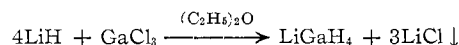
Experimental

Materials were handled in a conventional high-vacuum line or in a glove box under an atmosphere of oxygen-free dry nitro-

gen. All solvents, after preliminary desiccation, were dried over lithium hydride or lithium aluminum hydride and redistilled before use.

Trimethylamine hydrochloride was prepared by passing a stream of dry hydrogen chloride through an ethereal solution of the anhydrous base. The solid was filtered, washed with ether, and freed from traces of solvent under vacuum. Deuterium chloride, prepared by the action of deuterium oxide on benzoyl chloride,⁸ was used in the preparation of trimethylamine deuterium chloride. Gallium trichloride was prepared and purified as previously described.⁹

Lithium Gallium Hydride.—The method used was similar to that originally described.⁴ In a typical experiment finely ground lithium hydride (3.29 g., 415 mmoles) was slowly added to a magnetically stirred solution of gallium trichloride (4.53 g., 25.7 mmoles) in 50 ml. of ether at 0° using the apparatus shown in Fig. 1.



The solution was stirred for 12 hr. at room temperature and then filtered through the glass sinter to yield an ethereal solution of lithium gallium hydride which was used in subsequent experiments. LiGaD_4 was prepared similarly from lithium deuteride.

Trimethylamine Gallane.—Trimethylamine hydrochloride (0.67 g., 7.0 mmoles) was added at -196° to a slight excess of

TABLE I
DISSOCIATION PRESSURE OF $[(\text{CH}_3)_3\text{N}]_2\text{GaH}_3$

Temp., °C.	<i>p</i> , mm. (obsd.)	<i>p</i> , mm. (calcd.)
-28.0	41.8	42.0
-25.7	53.0	50.9
-24.5	57.0	56.5
-23.6	61.0	60.8
-22.3	67.0	67.6
-20.0	81.1	81.7
-18.2	93.0	94.8
-16.9	104.6	105.2
-15.4	116.7	118.0
-14.2	129.3	130.0
-13.2	139.3	140.6
-12.2	151.2	151.7
-11.0	166.7	166.4
-10.2	177.8	176.6
- 9.0	195.3	193.6
- 8.2	208.0	205.6
- 5.1	264.4	258.8
- 1.2	342.0	341.2

(7) D. Shriver, R. W. Parry, N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, **2**, 867 (1963).

(8) H. C. Brown and C. Groott, *J. Am. Chem. Soc.*, **64**, 2223 (1942).

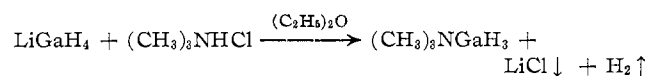
(9) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1527 (1956).

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 (3) N. N. Greenwood and K. Wade, "Friedel-Crafts Reactions," G. A. Olah, Ed., Interscience Publ., Inc., New York, N. Y., 1963.
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TABLE II
 INFRARED DATA FOR $(\text{CH}_3)_3\text{NGaH}_3$ AND $(\text{CH}_3)_3\text{NGaD}_3$

$(\text{CH}_3)_3\text{NGaH}_3$			$(\text{CH}_3)_3\text{NGaD}_3$			Ratio $\nu_{\text{H}}/\nu_{\text{D}}$	Assignment
ν , cm.^{-1}	$\Delta\nu_{1/2}$, cm.^{-1}	ϵ_{rel}	ν , cm.^{-1}	$\Delta\nu_{1/2}$, cm.^{-1}	ϵ_{rel}		
1853	18	1.00	1330	23	0.45	1.393	ν_1, ν_4 sym. and asym. Ga-H stretch
758	15	1.43	542	19	.41	1.398	
715	..	0.06	(510)	(1.40)	ν_2 sym. H-Ga-H def.
523	21	.07	ν_3 N-Ga \equiv H ₃ rock
488	}PQR	.07	487	}PQR	ν_3 Ga-N stretch
482		.085	479		.14	1.006	
475		.06	473		.10	1.004	

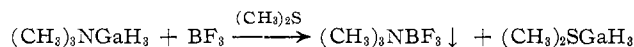
lithium gallium hydride (0.72 g., 8.9 mmoles) dissolved in ether; a simplified version of the apparatus shown in Fig. 1 was used in which the tap and ground joint shown at A were attached at B, A carried a B24 ground joint and stopper, and all the apparatus to the right of B was eliminated. The reaction, which commenced below -78° , was completed by stirring at 0° .



The volume of hydrogen evolved was measured using a Toepler pump (found 161 ml.; calcd. 157 ml. at S.T.P.). After removal of ether at -78° , the trimethylamine gallane was sublimed *in vacuo* from the reaction vessel at room temperature to a trap cooled to -78° where it collected as colorless needle-like crystals, m.p. 70.5° , vapor pressure approximately 2 mm. at room temperature. *Anal.* Calcd. for $(\text{CH}_3)_3\text{NGaH}_3$: Ga, 52.9; hydrolyzable H, 2.29; $(\text{CH}_3)_3\text{N}$, 44.8. Found: Ga, 52.3; hydrolyzable H, 2.32; $(\text{CH}_3)_3\text{N}$, 46.6. The complex decomposes over a period of weeks under vacuum at room temperature but is more stable under nitrogen. Complete thermal decomposition occurred at 150 – 180° to give gallium, hydrogen, and trimethylamine in the stoichiometric ratio 1.00:3.16:1.00, close to the expected ratio 1:3:1.

The trideuterio gallane derivative $(\text{CH}_3)_3\text{NGaD}_3$, m.p. 68.1° , was obtained similarly from lithium gallium deuteride, LiGaD_4 (0.1 g., 1.2 mmoles), and trimethylamine deuterium chloride, $(\text{CH}_3)_3\text{NDCl}$ (0.1 g., 1.0 mmole).

Displacement Reaction: Dimethyl Sulfide Gallane.—Boron trifluoride (0.70 g., 10.3 mmoles) was allowed to react at -15° with a stirred solution of trimethylamine gallane (1.35 g., 10.3 mmoles) in dimethyl sulfide.



After filtering the residue (identified as trimethylamine boron trifluoride by infrared spectrum and m.p. 138°) the colorless solution was fractionated *in vacuo* through a trap cooled to -78° . After removal of the excess solvent at -70° from this trap, dimethyl sulfide gallane remained as colorless crystals. *Anal.* Calcd. for $(\text{CH}_3)_2\text{SGaH}_3$: Ga, 51.7; hydrolyzable H, 2.24; $(\text{CH}_3)_2\text{S}$, 46.0. Found: Ga, 51.0; hydrolyzable H, 2.28; $(\text{CH}_3)_2\text{S}$, 46.7. No sharp melting point could be recorded, probably due to instability, since at room temperature the adduct decomposed to give dimethyl sulfide, hydrogen, and metallic gallium.

Analyses.—Two independent methods were used to analyze the adducts: (1) A weighed sample was hydrolyzed by water or aqueous methanol and the volume of hydrogen evolved was measured using a Toepler pump. The aqueous solution of the ligand was then determined by back-titration after distilling the solution into an excess of 0.1 M hydrochloric acid. The gallium remaining was either precipitated quantitatively as the 8-hydroxyquinoline complex and weighed or titrated with EDTA using xylenol orange as indicator.¹⁰ (2) The complex was thermally decomposed quantitatively at a suitable temperature and the hydrogen and metallic gallium determined as above. Trimethylamine and dimethyl sulfide were identified by their infrared spectra and determined gas-volumetrically using a con-

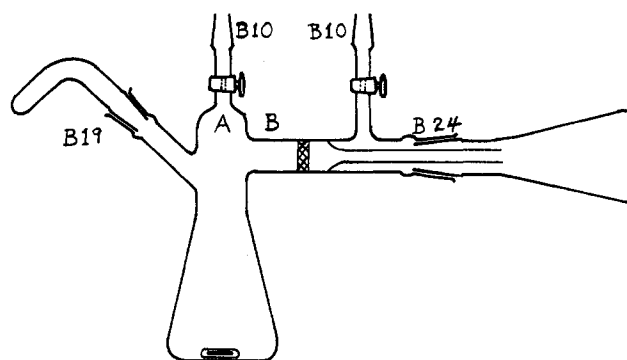
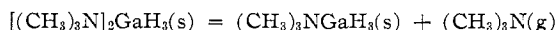


Fig. 1.—Reaction vessel.

stant-volume manometer on the vacuum line.

Tensiometric Titration of Trimethylamine Gallane with Trimethylamine.—Trimethylamine (1.31 g., 22.1 mmoles) was condensed onto trimethylamine gallane (0.38 g., 2.9 mmoles) in a reaction tube attached to the constant volume manometer. The reaction tube was immersed in a bath at -21° and the pressure in the system measured with a precision cathetometer as successive volumes of trimethylamine were removed. After correction for the amount of trimethylamine in the gas phase, values for the ratio of trimethylamine to trimethylamine gallane in the condensed phase were calculated. A plot showing the variation of pressure with the molar ratio of amine to amine gallane shows a sharp break near the ratio 1.0 indicating the presence of the 2:1 adduct $[(\text{CH}_3)_2\text{N}]_2\text{GaH}_3$ but no higher amine adducts. The curve, obtained independently at -21° , is essentially identical in form with that recorded simultaneously by Shriver and Parry. At temperatures between -21° and room temperature, 1 mole of trimethylamine could be removed quantitatively to leave the 1:1 adduct. The dissociation pressure for the equilibrium



was measured in the range -28 to 0° on a sample prepared by condensing the calculated amount of trimethylamine (2.90 mmoles) onto a weighed sample of the 1:1 adduct. The results are given in Table I and lead to the equation

$$\log p_{\text{mm}} = 10.867 - 2265/T$$

From this $\Delta H_{\text{dissoc}} = 10.35$ kcal./mole and $\Delta S_{\text{dissoc}} = 36.5$ e.u.

Infrared Spectra.—Spectra for the qualitative identification of compounds were obtained on Infracord Model 137 instruments using sodium chloride (4000 – 670 cm.^{-1}) and potassium bromide (800 – 400 cm.^{-1}) optics. Definitive spectra were recorded on a Grubb Parsons double-beam spectrometer.

Trimethylamine gallane and trimethylamine trideuterio gallane have vapor pressures of 2–3 mm. at room temperature and this is sufficient to enable their gas-phase infrared spectra to be recorded.¹¹ In addition to the weak bands directly attributable to the ligand, trimethylamine, the bands listed in Table II were also observed. The two bands with highest frequency were sharp and were by far the strongest features in the spectrum, being some twelve times as intense as the three strongest trimethylamine

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(11) N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Proc. Chem. Soc.*, 249 (1962).

bands at 2860, 1471, and 1012 cm^{-1} ; they shifted by a factor of $1/\sqrt{2}$ on deuteration. The band at lowest frequency exhibited a well defined PQR structure and remained unaltered on deuteration, implying that it was the Ga-N stretching mode. When the 1:1 adduct was dissolved in benzene, the observed bands were at 1830 (s) (plus a shoulder at 1795), 740 (s), 527 (s), and 488 (s) cm^{-1} . As expected, it was no longer possible to resolve the structure in the band at 488 cm^{-1} and the weak fundamental at 715 cm^{-1} became merged in the intense band at 740 cm^{-1} .

The infrared spectrum of the 2:1 adduct in benzene showed seven bands (see Table III) in addition to those of trimethylamine, which were in this case of comparable intensity to those of the gallane group.

TABLE III
INFRARED DATA FOR $[(\text{CH}_3)_3\text{N}]_2\text{GaH}_3$ IN BENZENE SOLUTION

ν , cm^{-1}	1850	1775	780	750	527	495	420
ϵ_{rel} (approx.)	1	0.4	0.3	0.9	1	1	0.1

Discussion

The infrared spectra of trimethylamine gallane and trimethylamine trideuteriogallane can be assigned as shown in Table II on the basis of a monomeric structure in which the gallium atom has approximately tetrahedral symmetry. The groups $\text{N} \rightarrow \text{GaH}_3$ and $\text{N} \rightarrow \text{GaD}_3$ then have local C_{3v} symmetry with six infrared-active modes. Only five bands are observed for the $\text{N} \rightarrow \text{GaH}_3$ group since the symmetric and asymmetric Ga-H stretching frequencies (ν_1 , ν_4) are not resolvable in the gas phase, though they are partially resolvable in solvents such as benzene, where the asymmetric mode appears as a shoulder on the low frequency side of the intense symmetric band. On deuteration, the Ga-H stretching frequency decreases by a factor close to $1/\sqrt{2}$; the Ga-D band has a similar shape and half band width but is only about half as intense. The position of these bands is very similar to those of the M-H and M-D stretching modes in $(\text{CH}_3)_3\text{NAlH}_3$, $(\text{CH}_3)_3\text{NAlD}_3$,^{12,13} and various heavy metal hydrides.^{14,15}

The bands at 758 and 715 cm^{-1} were assigned to the asymmetric and symmetric H-Ga-H deformations, respectively, by analogy with alanes and other comparable molecules.^{12,13,15} On deuteration, the asymmetric deformation ν_5 shifts by the expected factor of $1/\sqrt{2}$; it retains the same band shape and approximate half band width but drops in intensity by a factor of three. The corresponding ν_2 symmetric deformation has only one twenty-fourth the intensity of the asymmetric mode and this, coupled with the low vapor pressure of the compound and the further drop in intensity on deuteration, precluded the possibility of observing the weak D-Ga-D fundamental expected at about 510 cm^{-1} .

The assignment of the band at 482 cm^{-1} to the Ga-N stretching mode follows from the fact that this is the only band which does not shift on deuteration (though it does increase somewhat in intensity). The band also has the expected PQR structure (*cf.* the C-Cl stretching vibration in the analogous C_{3v} molecule ClCH_3).

The remaining band at 523 cm^{-1} must then be assigned to the $\text{N-Ga}\equiv\text{H}_3$ rocking mode (ν_6). Deuteration should diminish this frequency and the corresponding band was not observed for $(\text{CH}_3)_3\text{NGaD}_3$ since measurements were not made below 400 cm^{-1} , which corresponds to a ratio of only 1.3. A factor of 1.41 would lead to a predicted frequency of 370 cm^{-1} and it may be significant that a band was found at just this position in the Raman spectrum of $(\text{CH}_3)_3\text{NGaD}_3$ but not in $(\text{CH}_3)_3\text{NGaH}_3$.¹⁶ However, bands arising from rocking motions frequently show an isotope shift of significantly less than 1.41 so the unobserved band in the infrared spectrum might be between 370 and 400 cm^{-1} . An alternative interpretation¹⁷ of the Raman line at 370 cm^{-1} which would also account for its comparative sharpness would be its assignment to the symmetric $\text{N}(\text{CH}_3)_3$ deformation since this fundamental appears at 365 cm^{-1} in gaseous trimethylamine and consistently close to 380 cm^{-1} in the boron halide complexes.

The foregoing discussion establishes the complete assignment of the infrared spectrum of trimethylamine gallane on the basis of the monomeric structure $(\text{CH}_3)_3\text{-NGaH}_3$. The results also permit a detailed analysis of the closely related spectra of $(\text{CH}_3)_3\text{NAlH}_3$ and $(\text{CH}_3)_3\text{-NAlD}_3$ which have previously eluded complete assignment because of the ready disproportionation of the 1:1 adduct into the 2:1 adduct and alane,¹⁸ which itself subsequently decomposes. From this it appears that the Al-H and Al-D stretching modes (ν_1 and ν_4) occur at slightly lower frequencies than in the corresponding gallanes, whereas the ν_2 and ν_3 deformations and the N-AlH_3 rocking mode (ν_6) occur at slightly higher frequencies.

It was not possible to obtain a vapor-phase spectrum for the 2:1 adduct because of the ready decomposition under reduced pressure. In addition, the solution spectra have various complicating features so that the assignment of bands does not lead unambiguously to a detailed structure in this case. However, the simplicity of the spectrum argues for a monomeric structure. A trigonal bipyramid in which the three hydrogen atoms are equatorial has D_{3h} symmetry; this model has eight independent modes of vibration of which five are infrared-active. The appearance of seven bands in the solution spectrum suggests that the forbidden modes involving the symmetric GaH_3 stretch and the symmetric GaN_2 stretch may become allowed by interaction of the complex with the solvent. The dissociation of the 2:1 complex to give appreciable amounts of the 1:1 adduct or the presence of the two ligands in equatorial positions (eleven infrared-active modes) appear as less likely alternatives. Steric crowding renders improbable the configuration in which one ligand is equatorial and the other polar (twelve infrared-active modes).

The 2:1 complex, though it dissociates in the vapor

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(16) D. F. Shriver, R. L. Amster, and R. C. Taylor, *J. Am. Chem. Soc.*, **84**, 1321 (1962).

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phase below room temperature, appears to be comparable in stability to $[(\text{CH}_3)_3\text{N}]_2\text{GaCl}_3$ and $[(\text{CH}_3)_3\text{N}]_2\text{-GaBr}_3$, which are reported to revert slowly to the corresponding 1:1 adducts under vacuum at -48.7° ¹⁹; at this temperature $[(\text{CH}_3)_3\text{N}]_2\text{GaH}_3$ has a calculated dissociation pressure of 6.0 mm. The 2:1 compound is also comparable in stability to $[(\text{CH}_3)_3\text{N}]_2\text{AlCl}_3$, for which¹⁹ $\log p_{\text{mm}} = 9.70 - 2280/T$; the heat of dissociation of the aluminum chloride complex is therefore 10.43 kcal./mole, which is close to the value of 10.35 kcal./mole in the gallane adduct.

The 1:1 complex $(\text{CH}_3)_3\text{NGaH}_3$ is considerably less stable than $(\text{CH}_3)_3\text{NBH}_3$ but is similar in stability to $(\text{CH}_3)_3\text{NAlH}_3$ although the two compounds decompose in rather different ways due to the fact that the $[(\text{CH}_3)_3\text{N}]_2\text{AlH}_3$ is much more stable than $[(\text{CH}_3)_2\text{N}]_2\text{GaH}_3$. The m.p. of the 1:1 alane, 76° ,¹³ is also close to that of $(\text{CH}_3)_3\text{NGaH}_3$, 70.5° . As expected, the 1:1 complexes of alane and gallane are considerably less stable than the corresponding complexes of aluminum and gallium trihalides and they are also less stable than the com-

plexes of trimethylaluminum and trimethylgallium.²⁰

The preparation of $(\text{CH}_3)_2\text{SGaH}_3$ from $(\text{CH}_3)_3\text{-NGaH}_3$ involves the replacement of a strong ligand by a weaker one. This type of reaction is frequently useful and deserves to be better known. The technique is to displace the desired acceptor by a stronger acceptor using the weaker ligand as solvent. In general, the strong ligand combines with the stronger acceptor leaving the weak ligand and weak acceptor to combine; separation then depends on the particular properties of the two new complexes formed.

$(\text{CH}_3)_2\text{SGaH}_3$ decomposes at lower temperatures than does $(\text{CH}_3)_2\text{SGa}(\text{CH}_3)_3$ ²¹; however, its properties suggest that it is more stable than the corresponding etherates and this point is being further investigated.

Acknowledgments.—The authors gratefully acknowledge the award of a D.S.I.R. Maintenance Grant to A. S. and an I.C.I. Fellowship to M. G. H. W. tenable at the University of Nottingham, where much of this work was carried out.

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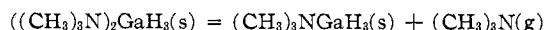
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Preparation and Characterization of Trimethylamine Gallane and Bistrimethylamine Gallane

BY D. F. SHRIVER AND R. W. PARRY

Received August 31, 1962

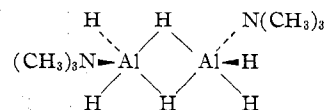
A new compound $(\text{CH}_3)_3\text{NGaH}_3$ (trimethylamine gallane) has been prepared and characterized. It is a volatile solid which decomposes upon standing at room temperature and is monomeric in dimethyl ether solution. Crystallographic evidence is presented which indicates the absence of a hydrogen bridge structure in the solid. It was found that trimethylamine gallane can take up a second mole of trimethylamine to form bistrimethylamine gallane. This latter compound is monomeric in trimethylamine solution and thus appears to contain a five-coordinated gallium atom. ΔH° and ΔS° for the reaction



at -31.05° are, respectively, 11.5 kcal./mole and 41.1 cal./mole-deg.

Amine adducts of BH_3 and AlH_3 have received considerable attention in the literature.¹⁻⁵ The alkyl amine addition compounds of BH_3 are typified by the monomeric compound $(\text{CH}_3)_3\text{NBH}_3$. By contrast, two points are of special interest with the amine-aluminum hydride derivatives. One is the partial dimerization of $(\text{CH}_3)_3\text{NAlH}_3$ and its related compounds in benzene solution.²⁻⁴ There is some controversy over the nature of the interaction involved in this dimerization. Both

a hydrogen-bridged structure



and dipole-dipole interactions have been proposed²⁻⁵ to account for the dimer. Another item of interest is the addition of two moles of trimethylamine to AlH_3 to give a compound containing a five-coordinated aluminum atom.^{4,6}

Since no data for the amine derivatives of GaH_3 were found in the literature, it was of interest to prepare and

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