ATRANES

XXXIII.* PMR SPECTRA OF METALLOATRANE-3,7,10-TRIONES CONTAINING A GROUP-IIIB METAL ATOM

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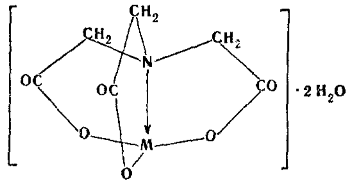
The PMR spectra of acidified solutions of metalloatrane-3,7,10-trione dihydrates $\overline{\mathrm{N(CH_2COO)_3}\overset{\downarrow}{\mathrm{M}}}\cdot 2H_2O$ containing a group-IIIB metal atom (M=Al, Ga, In, Tl) in D_2O were studied. The equivalence of the three atrane half-rings in all of the investigated molecules and of the methylene protons in each half-ring was proved. Spin-spin coupling of ^{203}Tl and ^{205}Tl with protons, which is apparently realized through a Tl←N transannular coordinate bond, is observed in the PMR spectrum of thallatrane-3,7,10-trione (M=Tl). The factors that determine the magnitudes of the chemical shifts of the methylene protons are discussed.

In one of our preceding communications [2], we described the synthesis of metalloatrane-3,7,10-triones containing a group-IIIB metal atom (I):



I

a M=Al; b M=Ga; c M=In; d M=Tl

The aim of the present communication was a study of the structure of I by means of PMR spectroscopy. Up until now, only a few publications [3-5] have been devoted to an investigation of the structure of metalloatrane-3,7,10-triones by PMR spectroscopy.

The PMR spectra of I† demonstrate that all of the investigated compounds are monomeric in aqueous solution and contain an intramolecular M←N bond [6].

The methylene protons in the PMR spectra of acidified solutions of I in D_2O ($pH \leq 3$) are represented (see Table 1) by a narrow singlet at τ 6.27 (Al), 6.23 (Ga), and 6.60 (In). This confirms the spectroscopic proof of the equivalence of the three $\overline{\overset{\downarrow}{\mathrm{M}}\mathrm{—O—CO—CH_2—N}}$ half-rings in their molecules [6]. The equivalence of the protons in each of the atrane half-rings indicates the presence of rapid conformational transi-

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* See [1] for communication XXXII.

† We were unable to obtain the spectrum of boratrane-3,7,10-trione (M=B), since it is only slightly soluble in water.

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TABLE 1. Chemical Shifts in the PMR Spectra of Metalloatrane-3,7,10-triones (I)

M	τ_{CH_2}, ppm
Al	6,27
Ga	6,23
In	6,60
Tl	6,42*

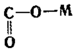
* Two doublets: $J_{^{205}TlH} = 387$ Hz, $J_{^{203}TlH} = 384$ Hz.

tions of these five-membered heterocycles that average the position of the protons of the methylene group relative to the C=O bond.

The PMR spectrum of thallatrane-3,7,10-trione is extremely interesting. The protons of the CH_2 groups in it are represented by two doublets with a common center at 6.42 τ. The ratio of the intensities of the lines of the doublets (7:3) corresponds to the natural ^{205}Tl and ^{203}Tl isotope ratio (the nuclear spin on each of them is 1/2). Consequently, the splitting of the lines of the methylene protons is due to their spin-spin coupling (SSC) with thallium-205 and 203 ($J_{^{205}Tl,H} = 387$ Hz, $J_{^{203}Tl,H} = 384$ Hz). This sort of coupling seems of particular interest. The high ionic character of the Tl–O bond in the thallatrane-3,7,10-trione molecule ($\varkappa_{Tl-O} = 85\%$) [6] should, in analogy with thallium triacetate, hinder participation of this bond in transfer of the SSC between the Tl and H nuclei through four bonds (Tl–O–CO–C–H). It can therefore be assumed that the indicated coupling in thallatrane-3,7,10-trione is realized through three bonds (Tl←N–C–H).

The participation of a Tl←N coordinate bond in transfer of the SSC between the Tl nuclei and the protons of the methylene group attached to the nitrogen atom has already been proved in intermolecular organic complexes of thallium with amines [7]. However, our observed case of this sort of coupling, which is transmitted through an intramolecular M←N bond, has been detected for the first time.

The chemical shifts of the methylene protons in the PMR spectra of I characterize the strength of the M←N bonds in their molecules to a lesser extent than the τ_{NCH_2} value in the spectra of metalloatranes [8, 9]. This is due to the substantial contribution of the magnetic anisotropy of the C=O bonds to the shielding constants of the methylene group protons. This contribution should depend on the nature of the M atom, owing to the difference in the electronic structure of this bond (the ionic character of the M–O bond and the character of the M–O bonds and the electronegativity of the M atom) in their molecules and also to the dissimilar relative position of the C=O bonds and protons (because of the change in the three-dimensional structure of molecules of I on passing from M=Al to M=Tl).

In addition, the τ_{CH_2} values of I should depend on the state of the  $\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}O{-}M$ grouping.

All of this makes it impossible to sufficiently reliably determine the order of the change in the strength of the M←N bonds in the investigated compounds.

Nevertheless, the appreciably larger shielding of the methylene protons in the PMR spectra of Ic and Id (M=In, Tl) as compared with Ia and Ib (M=Al, Ga) is in agreement with the IR-spectroscopic data [6, 10], which show that the donor–acceptor interaction between the M and N atoms weakens as the atomic number of M in I increases.

The PMR spectra of I in aqueous solutions with higher pH values (5-7) attest to appreciable hydrolysis of these compounds to free aminotriacetic acid. A similar phenomenon was previously studied in detail in the case of 1-hydroxy-1-oxomolybdatrane-3,7,10-trione [3-5].

EXPERIMENTAL

The synthesis of the starting metalloatrane-3,7,10-triones was previously described in [2].

The PMR spectra of acidified saturated solutions of I in D_2O (pH 1-3) were obtained with a Perkin-Elmer R-12A spectrometer (60 MHz) at 36° with tert-butyl alcohol as the internal standard. The chemical shifts were measured with an accuracy of ± 0.02 ppm and are presented on the τ scale.

The pH values of the solutions were determined with an LPU-01 pH meter with a glass electrode at 20 ± 1°.

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