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Spectra and structure of mercury derivatives of primary nitramines

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The mercury derivatives of primary nitramines were proved by molecular spectroscopy and quantum-chemical calculations to be covalent compounds. The mercury atom was found to be coordinated to the amine nitrogen atom.

Key words: IR spectroscopy, Raman spectroscopy, UV spectroscopy, quantum-chemical calculations, molecular structure, primary nitramines, mercury derivatives.

The structure of mercury(II) complexes with nitramine ligands remains unclear to date. It could be assumed *a priori* that the mercury derivatives can exist in either the ion form in which the mercury(II) cation coordinates the anions of primary nitramines or in the covalent form, by analogy to the mercury derivatives of *C*-nitro compounds[1,2] in which the Hg atom is bound to the amine N atoms of the nitramine fragments or to the O atoms. The spectral distinctions of the ionic and covalent forms of nitramines are known.[3] This promped us to solve the problem of the structure of such compounds using spectral methods.

In this work, with the purpose to reveal the specific features of the structure of the mercury derivatives of primary nitramines, we obtained and examined the IR, Raman, and UV spectra of methylnitramine (**1**), ethylenedinitramine (**2**), and phenylsulfonitrylamine derivatives (**3**) and performed the quantum-chemical calculations of structure **1**.

Results and Discussion

The Raman and IR spectra of compounds **1—3** were recorded under different conditions. For compound **1** we synthesized the isotopomer with ^{15}N in the nitro group and studied its characteristics. The main data are presented in Table 1.

Examining the spectra, we used the following prerequisites. For the ionic form, the vibrational spectra of compounds **1—3** correspond to those of primary nitramines,[4,5] which are characterized by intense absorption bands in the 1460—1490 cm^{-1} region.* In the case of the covalent structure, strong bands in the IR spectral region higher than 1500 cm^{-1} ($\nu_{az}(NNO_2)$) characteristic of nitramines or their O-esters should be observed.[6,7] The IR spectra of compounds **1**, **2**, and **3** in KBr pellets almost completely coincide with the spectra of potassium salts of methyl-, ethylenedi-, and phenylsulfonylnitramines, respectively. The band frequencies in the IR spectra of suspensions of **1—3** in Nujol on the KBr and Ge plates are close to those for the nitramine salts. The same concerns the spectra of these suspensions on CaF_2 plates, except for compound **3**. The data obtained can indicate cation exchange in the case of compounds **1** and **2**.

In the IR spectra of a suspension of **3** in Nujol (CaF_2 plates) and a solution of **3** in CH_2Cl_2 (CaF_2 cell), the band frequencies coincide with line frequencies in the Raman spectrum of this compound in the crystalline phase, which confirms the absence of exchange. Therefore, the main conclusions on the structure were drawn from the IR spectra for compound **3**.

The IR spectra of compound **3** differ substantially from those of the nitramine salts and are closer to the spectra of secondary nitramines.[3,6] The intense band in the region higher than 1500 cm^{-1} is especially significant and allows the conclusion about the covalent structure of compound **3**.

In the case of compounds **1** and **2**, prominence was given to the Raman spectra. Examination of the Raman spectra of **1—3** and comparison with the spectra of nitramines and their salts showed that they differ from the spectra of the nitramine salts and correspond better

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† Deceased.

* For the salts with the Li and Na cations, these bands lie higher than 1500 cm^{-1}.

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Table 1. Vibrational spectra[a] (ν/cm^{-1}) of mercury nitramine derivatives **1—3**

1, Raman			**2**, Raman[b]	**3**		
I[b]	II[c]	III[d]		IR		Raman[b]
				I[b]	II[e]	
				1585 v.w	1585 p	1585 s
1550 w	1508 w	1550 w, dp	1550 w	1550 s	1555 s	1550 w
1537 w	1493 w		1540 w	1520 w		1523 w
1445 w	1445 w	1445 w, dp	1458 w			1454 w
1435 w	1435 w		1420 w			
1413 w		1413 w, dp	1409 w			
1399 w	1371 m		1374 w	1340 s	1370 m	1345 w
1300 w.br	1284 w.br		1303 w	1290 s		1290 s
1193 w	1189 w	1192 w, p		1190 w		1185 m
1154 s	1144 s	1157 m, p	1157 s	1165 s	1180 s	1165 s
1146 s	1139 s		1122 w			
				1088 m	1090 w	1086 m
						1029 m
						1016 m
974 v.s	971 v.s	975 s, p	965 v.s			1002 v.s
			934 w			939 w
780 v.w	780 v.w		776 w			774 s
746 w	739 w		760 w			759 w
737 s	731 s	736 m, p	727 m			725 w
641 m						
634 w	635 m	637 m, p	621 w			613 m
						594 m
						568 w
						471 w
			437 w			443 w
404 m	400 m					415 m
						349 m
			315 w			325 m
286 w			287 w			
			265 m			
249 m	242 m		243 w			231 m
						205 w
152 m	150 s		169 s			171 w
			140 m			
118 m	116 s		129 m			117 s
						111 s
			86 s			84 s
78 m						75 m
67 s.br	65 s		62 m			65 m
56 p	53 s					
50 p			46 m			40 m
28 m	28 s					36 m
25 m	25 s					26 m
18 s			20 s			

[a] The following designations were used: w, m, and s are weak, medium, and strong bands, respectively; v is very, br is broad; and p and dp are polarized and depolarized Raman lines, respectively.

[b] Solid sample.

[c] Isotope-substituted (^{15}N) sample in the solid state.

[d] Solution in H_2O.

[e] Solution in CH_2Cl_2.

to those of nitramines.[3—6] The most important feature is the presence of lines in the frequency region >1500 cm^{-1} in the Raman spectra of compounds **1—3**, namely, 1537, 1550 cm^{-1} (**1**); 1540, 1550 cm^{-1} (**2**); 1523, 1550 cm^{-1} (**3**). At the same time, the spectra of the nitramine salts contain no lines with the frequencies higher than 1500 cm^{-1} attributed to vibrations of the nitramine fragment. The line at 1585 cm^{-1} in the Raman spectra of both compound **3** and potassium salt of phenylsulfonylnitramine is assigned to the benzene ring vibration. The isotope substitution in the nitro group of molecule **1** for ^{15}N gives the low-frequency shift for these lines by 44 and 42 cm^{-1}, respectively. The line at 1550 cm^{-1} in the Raman spectrum of a saturated aqueous solution of compound **1** is depolarized despite a possible partial dissociation, whereas in the Raman spectra of the nitramine salts the lines in the 1470—1480 cm^{-1} region attributed to symmetric stretching vibrations of the nitramine fragment are polarized.[3—5]

The data on the IR and Raman spectra of compounds **1—3** suggest that the observed intense bands in the IR spectra in the region higher than 1500 cm^{-1} (for **3**) and the corresponding weak, depolarized lines in the Raman spectrum (for **1—3**) with an isotope shift of ~40 cm^{-1} (lines in the spectrum of **1**) are attributed to the antisymmetric stretching vibrations of the nitramine fragment ($\nu_{az}(NNO_2)$). This fact indicates the covalent structure of molecules **1—3**. Since the frequencies and the spectral pattern for compounds **1—3** correspond to nitramines better than to their O-esters, we believe that the Hg atom is more likely bound to the amine N atom of the nitramine fragment.

The covalent structure of compounds **1—3** is also favored by the data of their UV spectra. The UV spectrum of the crystalline film of compound **1** contains a strong band at λ_{max} = 255 nm, and the spectrum of an aqueous solution of **1** exhibits the shift to 246 nm (ε = 12400). On 100-fold diluting the shift increases to 232 nm (ε = 14300). The absorption band remains unchanged (λ_{max} = 229 nm, ε = 7600) for alkaline methylnitramine salts in both the crystalline state and aqueous solutions.

Thus, it follows from analysis of the IR, Raman, and UV spectra that the mercury derivatives of primary nitramines are covalent and, probably, the Hg atom is bound to the amine N atom of the nitramine fragment.

However, the covalent structure of the mercury derivatives of primary nitramines can be different. Using quantum-chemical methods, we attempted to establish to which atom the Hg atom coordinates. The structure of the $Hg(NMeNO_2)_2$ molecule was calculated by the B3LYP method in the CEP-121G basis set. According to the results obtained, the above assumption is confirmed. The structure in which the Hg atom is coordinated to the amine N atoms is by 12 kcal mol^{-1} more favorable than that with coordination to the O atom (or atoms).

Table 2. Main structural parameters of mercury methylnitramine derivative **1** calculated by the B3LYP method in the CEP-121G basis set

Bond	d/Å	Angle	ω/deg
Hg—N	2.08	N—Hg—N	180
N—N	1.38	C—N—Hg	133
C—N	1.48	N—N—Hg	110
N—O(1)	1.32	C—N—N	117
N—O(2)	1.29	O(1)—N—N	116
C—H	1.097	O(2)—N—N	120
C—H	1.093	O—N—O	125
C—H	1.097		
Hg—O(1)	2.77		
Hg—O(2)	4.12		

The main results on the structure of the $Hg(NMeNO_2)_2$ molecules are presented in Table 2 and Fig. 1. According to the calculation, the structure of $Hg(NMeNO_2)_2$ consists of two equivalent parts. The N, Hg, N atoms lie on the same straight line. Seven atoms, *viz.*, C, N, N, Hg, N, N, C, lie in the same plane. The N—O bond lengths in the nitro group differ, and the O—N—N angles also differ.

Using the quantum-chemical calculation, we obtained the force field of the $Hg(NMeNO_2)_2$ molecule and used it to determine the frequencies in the spectrum and shapes of vibrations. However, the correspondence of some cal-

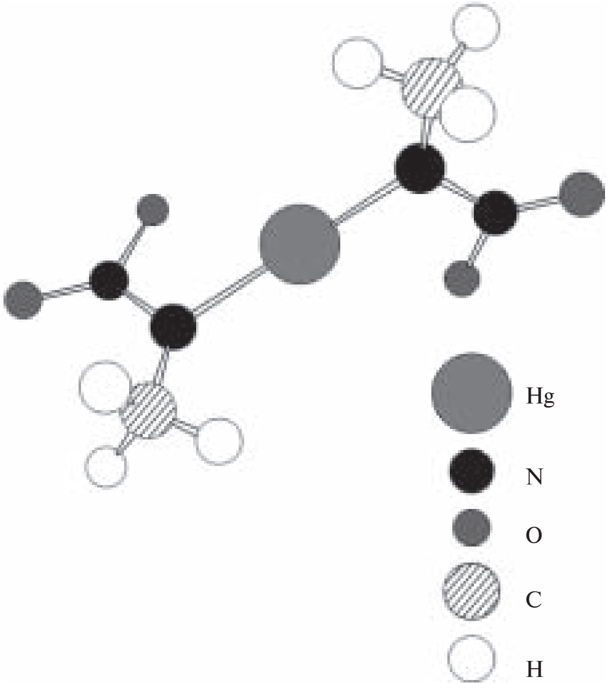

Fig. 1. Structure of molecule **1**.

culated frequencies to the experimental values was unsatisfactory. First, this concerns the stretching vibrations of the nitro groups, whose frequencies are noticeably underestimated (ν(NO) ~1406 cm^{-1}). The other frequencies lie in the expected regions. For example, ν(CN) is ~1120 cm^{-1} (two frequencies), ν(NN) is 923 and 927 cm^{-1}, and ν(N—Hg) is 266 and 370 cm^{-1}.

Experimental

IR spectra were recorded on a Specord M-80 spectrophotometer (KBr pellets, suspensions in Nujol on the KBr, Ge, and CaF_2 plates, and solutions in CaF_2 cells). Raman spectra were obtained on a Ramanor HG-2 spectrometer with an Ar laser as an excitation source. UV spectra were recorded on a Specord M-40 spectrophotometer.

Quantum-chemical calculations were performed using the GAUSSIAN-98 program by the B3LYP method in the CEP-121G basis set.[8]

Compounds **1—3** were synthesized using known procedures.[9—11] The isotopomer with ^{15}N in the nitro group was prepared as described previously.[12]

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