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The Structure of Triazenato-Mercury Compounds in Solution

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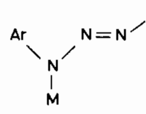
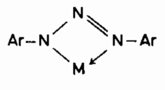
Metal–ligand spin–spin coupling has been used to look at structures of $ArN_3(HgC_6H_5)Ar'$ (1) and $(ArN_3Ar')_2Hg$ (2) in solution. ^{15}N and ^{199}Hg NMR data indicate intermolecular C_6H_5Hg exchange for 1 *(Ar = 2-pyridinyl) and π-triazaallyl-bonding or σ-triazaallylstructures associated with rapid intramolecular C_6H_5Hg exchange between N(1) and N(3) in other diaryltriazenes for compound types* 1 *and* 2. *^{199}Hg resonances are broadened by scalar relaxation of the second kind of the adjacent ^{14}N.*

Introduction

Considerable interest in the bonding properties of the triazenato ligand has developed in the past few years. As shown by X-ray diffraction techniques, the group may act as mono-(structure I) [1] or bidentate [2] (structure III) ligand in mononuclear complexes or as a bridging group between two metal centers [3].


I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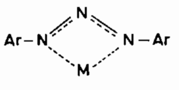

III

In solution, the bonding mode of the ligand has been studied by means of NMR: The equivalence of the aromatic ring protons or *para* Me, MeO or F groups [4–8] in symmetric diaryl-triazenato ligands has been used as a criterion of structure III or rapid intramolecular metal exchange between the terminal nitrogen atoms of the triazenato ligand in the asymmetric structures I and II or intermolecular ligand exchange.

This paper deals with spin–spin coupling between ^{199}Hg and ^{19}F or ^{15}N atoms in the ligand in triazenato–mercury compounds and its use in solution structure assignment of these compounds.

Mercury forms stable compounds with triazenato-ligands in bistriazenato–mercury and organomercury–triazenato compounds. The bonding mode in these compounds seems to be not yet established: Whereas the equivalence of all nitrogen atoms in solid bistriazenato–mercury compounds was suggested [9] to account for only one XPS N 1s signal, an X-ray structure determination [10] of [1-(2 chlorophenyl)-3-phenyl-1-triazenato-N^3] phenyl-mercury (*2b*) revealed a σ-triazaallyl like structure (II) with coordination of N(1) to the mercury atom. The effect of the asymmetric substitution of the triazene on the Hg–N bond lengths (Hg–N(1): 2.46 Å, Hg–N(3): 2.14Å) is however difficult to assess.

In solution, magnetic equivalence on the NMR time scale of the Me [11] and F [12] groups in *3b* and *4b* respectively has been observed and interpreted as discussed above. No temperature dependence of the spectra down to very low temperatures has been observed. Both inter- and intramolecular C_6H_5Hg exchange has been proposed for various phenyl-triazenato–mercury compounds [13].

$ArN_3(HgC_6H_5)Ar'$	Ar	Ar'	No*
	phenyl	phenyl	*1b*
	2-chlorophenyl	phenyl	*2b*
	4-methylphenyl	4-methylphenyl	*3b*
	2-fluorophenyl	2-fluorophenyl	*4b*
	2-fluorophenyl	phenyl	*5b*
	2-fluorophenyl	2-chlorophenyl	*6b*
	2-fluorophenyl	2-nitrophenyl	*7b*
	2-fluorophenyl	2-pyridinyl	*8b*
	phenyl	2-pyridinyl	*9b*

*the corresponding triazenes are signed with *a*, the corresponding bistriazenato–mercury compound with *c*.

Experimental

^{15}N and ^{199}Hg NMR spectra were recorded in the FT-mode on a Bruker WP-80 multinuclear spectrometer. Unless otherwise stated, the measurements were carried out using 0.5 *M* solutions in pyridine at 300 K. The temperatures were adjusted with a Bruker B-VT-1000. Chemical shifts were measured to high frequencies of external aniline ^{15}N (and converted [14] to the reference liquid ammonia at 25 °C) and external aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$). The mass spectra were obtained on a Varian Mat CH7 (70 eV), the chemical analysis on a Heraeus EA 415.

The triazenes not described in the literature (*5a*–*8a*) were prepared in the usual way [15] by reaction of the aryldiazonium salt with the corresponding aniline. The new bistriazenato–mercury compounds *5c–9c* were synthesized analogously to bis(1,3-diphenyl-1-triazenato-N)mercury [16]. The new phenyl triazenato–mercury compounds *5b–9b* were obtained by synproportionation [17] of the corresponding bistriazenato–mercury compounds and diphenyl mercury. Compounds *1a–1c* have been prepared as the isotopically normal compounds [11, 16, 18] using ^{15}N enriched (greater than 99.3 atom %) aniline from Stohler Isotope Chemicals. *4a–4c* [11, 17] and *9a* [19] were prepared according to literature methods.

$$HgT_2 + Hg(C_6H_5)_2 \longrightarrow 2THgC_6H_5, \; TH = \text{triazene}$$

*1,3-Diphenyl-1-triazene-1,3-$^{15}N_2$, (*1a*)*

$\delta(^{15}N)$ 0.5 *M* in DMSO: 373.5 (imino), 184.0 (amino), $^1J(^1H–^{15}N)$: 96 Hz $\delta(^{15}N)$ 0.5 *M* in toluene: 277.0 ppm.

*[(1,3-Diphenyl-1-triazenato-1,3-$^{15}N_2$)-N^3]phenyl-mercury, (*1b*)*

$\delta(^{15}N)$: 291.0 ppm, $\delta(^{199}Hg)$: 1221 ppm, $J(^{15}N–^{199}Hg)$: 169(300 K), 186 Hz (233 K).

*Bis[(1,3-diphenyl-1-triazenato-1,3-$^{15}N_2$)-N]mercury, (*1c*)*

$\delta(^{15}N)$ 0.25 *M* in pyridine: 285.3 ppm, $\delta(^{199}Hg)$ 0.25 *M* in pyridine: 720 ppm, $J(^{15}N–^{199}Hg)$: 386 Hz.

[1,3-Bis(2 fluorophenyl)-1-triazenato-N^3]phenyl-mercury, (4b)

$\delta(^{199}Hg)$: 1149 ppm, $J(^{19}F–^{199}Hg)$: 45 Hz.

*Bis[1,3-bis(2 fluorophenyl)-1-triazenato-N]mercury, (*4c*)*

$\delta(^{199}Hg)$: 574 ppm, $J(^{19}F–^{199}Hg)$: 80 Hz (263 K).

*1-(2 Fluorophenyl)-3-phenyl-1-triazene, (*5a*)*

Yellow crystals; mp.: 86 ℃. *Anal.* for $C_{12}H_{10}FN_3$: Calc. C, 67.0; H, 4.7; N, 19.5%; Found C, 67.1; H, 4.7; N, 19.6%.

*[1-(2 Fluorophenyl)-3-phenyl-1-triazenato-N]phenyl-mercury, (*5b*)*

Yellow crystals; mp.: 165 ℃. $\delta(^{199}Hg)$: 1184 ppm $J(^{19}F–^{199}Hg)$: 49 Hz. *Anal.* for $C_{18}H_{14}FHgN_3$: Calc. C, 44.0; H, 2.9; N, 8.5%; Found C, 44.2; H, 2.8; N, 8.6%.

*Bis[1-(2 fluorophenyl)-3-phenyl-1-triazenato-N]mercury, (*5c*)*

Yellow crystals; mp.: 210 ℃ (dec.). *Anal.* for $C_{24}H_{18}F_2HgN_6$; Calc. C, 45.8; H, 2.9, N, 13.4%. Found C, 46.0; H, 2.7; N, 13.0%.

*1-(2 Chlorophenyl)-3-(2 fluorophenyl)-1-triazene, (*6a*)*

Yellow crystals; mp.: 66 ℃. *Anal.* for $C_{12}H_9ClFN_3$; Calc. C, 57.7; H, 3.6; N, 16.8%; Found C, 58.1; H, 3.8; N, 16.7%.

*[1-(2 Chlorophenyl)-3-(2 fluorophenyl)-1-triazenato-N]phenyl-mercury, (*6b*)*

Yellow crystals; mp.: 158 ℃, $\delta(^{199}Hg)$: 1170 ppm, $J(^{19}F–^{199}Hg)$: 61 Hz. *Anal.* for $C_{18}H_{13}ClFHgN_3$; Calc. C, 41.1; H, 2.5; N, 8.0%; Found C, 41.2; H, 2.4; N, 8.1%.

*Bis[1-(2 chlorophenyl)-3-(2 fluorophenyl)-1-triazenato-N]mercury, (*6c*)*

Orange crystals; mp.: 172 ℃. *Anal.* for $C_{24}H_{16}Cl_2F_2HgN_6$; Calc. C, 41.3; H, 2.3; N, 12.0%; Found C, 41.4; H, 2.2; N, 12.1%.

*1-(2 Fluorophenyl)-3-(2 nitrophenyl)-1-triazene, (*7a*)*

Yellow crystals; mp.: 135 ℃. *Anal.* for $C_{12}H_9FN_4O_2$; Calc. C, 55.4; H, 3.5; N, 21.4%; Found C, 55.6; H, 3.5; N, 21.8%.

*[1-(2 Fluorophenyl)-3-(2 nitrophenyl)-1-triazenato-N]phenyl-mercury, (*7b*)*

Orange crystals; mp.: 165 ℃, $\delta(^{199}Hg)$: 1138 ppm $J(^{19}F–^{199}Hg)$: 93 Hz. *Anal.* for $C_{18}H_{13}FHgN_4O_2$; Calc. C, 40.3; H, 2.4; N, 10.4%; Found C, 40.4; H, 2.5; N, 10.5%.

*Bis[1-(2 fluorophenyl)-3-(2 nitrophenyl)-1-triazenato-N]mercury, (*7c*)*

Red crystals; mp.: 205 ℃. *Anal.* for $C_{24}H_{16}F_2N_8$-HgO_4; Calc. C, 40.1; H, 2.2; N, 15.6%; Found C, 40.1; H, 2.2; N, 15.7%.

*1-(2 Fluorophenyl)-3-(2-pyridinyl)-1-triazene, (*8a*)*

Yellow crystals; mp. 179 ℃. Mass spectrum: M^+ 6%, $(M–F)^+$ 1%, $(M–N_2)^+$ 3%, $(M–N_2, F)^+$ 6%, $(FC_6H_4N_2)^+$ 64%, $(FC_6H_4)^+$ 100%, $(C_6H_4)^+$ 32%, and others. *Anal.* for $C_{11}H_9FN_4$; Calc. C, 61.1; H, 4.2; N, 25.9%; Found C, 61.2; H, 4.3; N, 25.8%.

*[1-(2 Fluorophenyl)-3-(2-pyridinyl)-1-triazenato-N]-phenyl-mercury, (*8b*)*

Yellow crystals; mp. 148 ℃. $\delta(^{199}Hg)$ 1186 ppm. Mass spectrum, only Hg containing fragments: M^+ 50%, $(M–N_2)^+$ 14%, $(M–N_2, F)^+$ 27%, $(M–N_2, C_6H_5)^+$ 29%, $(C_6H_5)_2Hg^+$ 30% (product of thermal symmetrization), $C_6H_5Hg^+$ 100%, and others. *Anal.* for $C_{17}H_{13}FHgN_4$; Calc. C, 41.4; H, 2.7; N, 11.4%; Found C, 41.4; H, 2.7; N, 11.5%.

*Bis[1-(2 fluorophenyl)-3-(2-pyridinyl)-1-triazenato-N]mercury, (*8c*)*

Yellow crystals; mp.: 200 ℃ (dec.). *Anal.* for $C_{22}H_{16}F_2HgN_8$; Calc. C, 41.9; H, 2.6; N, 17.8%; Found C, 42.3; H, 2.4; N, 16.8%.

Phenyl[1-phenyl-3-(2-pyridinyl)-1-triazenato-N] mercury, (9b)

Yellow crystals; mp.: 137 °C, $\delta(^{199}Hg)$: 1198 ppm. *Anal.* for $C_{17}H_{14}HgN_4$; Calc. C, 43.0; H, 3.0; N, 11.8%; Found C, 43.1; H, 2.9; N, 11.9%.

Bis[1-phenyl-3-(2-pyridinyl)-1-triazenato-N] mercury, (9c)

Yellow crystals; mp.: 210 °C (dec.). *Anal.* for $C_{22}H_{18}HgN_8$; Calc. C, 44.4; H, 3.0; N, 18.8%; Found C, 44.4; H, 3.2; N, 18.8%.

Results and Discussion

The ^{199}Hg ($I = 1/2$) $\{^1H\}$ NMR spectrum of *4b* is a 1:2:1 triplett. This requires coupling of the mercury atom with two equivalent fluor atoms. This equivalence is due either to a π-triazaallyl-structure (III) or to rapid intramolecular C_6H_5Hg group exchange between N(1) and N(3) of the ligand in structure II: The four lines spectrum (neglecting $^2J(^{15}N-^{15}N)$) caused by coupling of the mercury with two different fluor atoms (structure II) would change according to the exchange matrix [20] given below into a 1:2:1 triplett with an appearant coupling constant of $(^4J + {}^6J)/2$.

$$\begin{matrix} 0 & 0 & 0 & 0 \\ 0 & -k & k & 0 \\ 0 & k & -k & 0 \\ 0 & 0 & 0 & 0 \end{matrix}$$

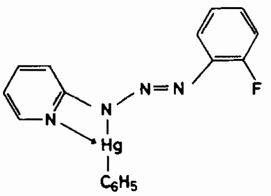
The observation of spin–spin coupling demonstrates the kinetic stability of the triazenato–mercury bond on this NMR time scale. Besides this, a mixture of two different phenyl-triazenato–mercury compounds displays two resonances even at very small differences in chemical shift. There is thus no DNMR spectroscopic evidence for the occurrence of intermolecular ligand exchange.

Additional information was expected from ^{199}Hg NMR spectra of compound *5b* containing only one fluor atom: In the case of a fixed σ-triazaallyl structure corresponding to the solid state structure [10] of *2b*, the coupling constant should be markedly smaller (^6J) compared with the coupling constant of *4b*. The separation of the dublett noted for *5b* is however very similar to the coupling constant of *4b* and indicates thus fluxional behaviour of *5b*.

Corresponding results have been obtained for *6b* and *7b*. The increase in coupling constant for *7b* is more reasonably explained by the electronegative substitution of the triazene than by a fixed structure II.

The addition of the triazene *6a* to a solution of the corresponding phenyl-triazenato–mercury compound *6b* (0.25 *M* *6a* and 0.5 *M* *6b* in pyridine) had no effect on the $^{19}F-^{199}Hg$ coupling pattern of *6b*. In contrast to the system $(2MeC_6H_4)_2N_3H/(2MeC_6H_4)_2N_3(HgC_6H_5)/C_6H_5Cl$ [13] the exchange of the proton and the phenyl–mercury group appears thus to proceed rather slow.

In contrast to *4b–6b* no coupling pattern could be discerned in a ^{199}Hg NMR spectrum of *8b*. This may be caused by rapid (intermolecular) triazene ligand exchange or fixed structure IV associated with an unobserved $^6J(^{19}F-^{199}Hg)$. The first possibility is supported by only one broadened line displayed in a mixture of *8b* and *9b*, indicating thus triazene ligand exchange. This exchange is possibly initiated by coordination of the pyridine nitrogen at the mercury atom of an other molecule.



IV

The ^{199}Hg NMR signals of compounds containing Hg–N bonds exhibit marked linebroadening. Scalar relaxation of the second kind [20, 21] of ^{199}Hg by the adjacent quadrupolar ^{14}N nucleus is proposed to be responsible for this effect taking into account the following reasons:

(*i*) The ^{199}Hg NMR linewidth of *4b* sharpen noticeably on cooling. This is thought to be caused by the decrease of the ^{14}N relaxation time along with decreasing correlation times, bringing about more effective N–Hg decoupling.

(*ii*) A temperature dependent change in rate would effect only the linewidth of the central peak of *4b* according to the exchange matrix given above, whereas the decrease in linewidth was found to apply uniformely to all three resonances of *4b*.

(*iii*) Furthermore the ^{199}Hg NMR lineshape of compound *1b*, the phenyl–mercury derivative from diphenyltriazene fully ^{15}N labeled in N(1) and N(3) was found to be field inhomogeneity determined. The estimation of the ^{14}N relaxation time assuming scalar relaxation of the second kind and using the $^{14}N-^{199}Hg$ coupling constant obtained [22] from $J(^{15}N-^{199}Hg)$ of *1b* yields reasonable values [22].

Besides this, the ^{15}N and ^{199}Hg NMR data of *1b* corroborate the results from *4b* concerning the bonding mode of the triazenato ligand. The $^{15}N-^{199}Hg$ coupling constant derived from ^{199}Hg and ^{15}N spectra is in the region of other ^{15}N-metal coupling constants [23–26]. The ^{15}N resonance lies in the middle of the amino and the imino nitrogen chemical shifts of the corresponding triazene (see below). Apart from a slight increase in $J(^{15}N-^{199}Hg)$, the spectra of *1b* did not change down to 233 K.

The bonding mode of the triazenato ligands in bistriazenato–mercury compounds appears to be the same as in organomercury–triazenato compounds discussed above, as can be seen from ^{15}N and ^{199}Hg spectra of compounds *1c* and *4c*. The equivalence of all four terminal nitrogen atoms of both ligands in *1c* is demonstrated by only one ^{15}N resonance. The ^{199}Hg NMR spectrum of *1c* is a quintett, which may be explained again by π triazaallyl bonding of both triazenato ligands or by metal exchange according to the following exchange matrix [20] in structure II.

$$\begin{matrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -k & 0 & k & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -k & 0 & 0 & 0 & k & 0 & 0 \\ 0 & k & 0 & -k & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -k & 0 & k & 0 \\ 0 & 0 & k & 0 & 0 & 0 & -k & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & k & 0 & -k & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$$

The same applies to the ^{199}Hg NMR spectrum of *4c* below 263 K. At room temperature *4c* displays a broad unresolved band due to reasons discussed above.

The larger coupling constants $J(^{15}N-^{199}Hg)$ and $J(^{19}F-^{199}Hg)$ observed for *1c* and *4c* compared with *1b* and *4b* reflect the difference in *trans* influence [27] between a phenyl and a triazenato group.

The ^{15}N NMR spectrum of *1a*, isotopically enriched in N(1) and N(3), in DMSO is a dublett of the amino nitrogen coupled to the attached proton and a singlet of the azo nitrogen. The ^{15}N chemical shifts were found to be almost identical to those of 3,3-dimethyl-1-phenyl-1-triazene [28]. The one bond $^{1}H-^{15}N$ coupling constant falls into the region of trigonal bonding to nitrogen [13]. There is thus no evidence for proton exchange in DMSO. On the other hand in toluene only one broad signal (bandwidth at halfheight 150 Hz) indicates intermolecular proton exchange.

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