Synthesis and spectral characteristics of organometallic derivatives of 2-thioquinazolinone: influence of metallation on tautomerism

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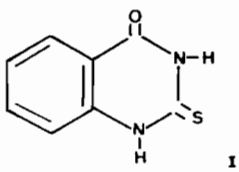
Abstract

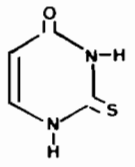
The compounds R_nMHTQ (R = Me, Ph; $n = 1$ (M = Hg), 2 (M = Tl); H_2TQ = 2-thioquinazolinone) and $(RHg)_2TQ$ (R = Me, Ph) have been prepared and their coordinative characteristics studied using vibrational (IR and Raman) and NMR (^1H, ^{13}C, ^{205}Tl) spectroscopy. Spectroscopic data in DMSO solution indicate that these complexes are closer to the enol form than the corresponding derivatives of 2-thiouracil.

Introduction

2-Thioquinazolinone (2-mercapto-4-(3*H*)-quinazolinone, H_2TQ, **Ia**) is a heterocyclic molecule related to 2-thiouracil (H_2Tu, **Ib**).

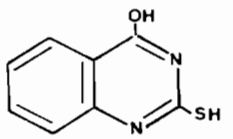


Ia



Ib

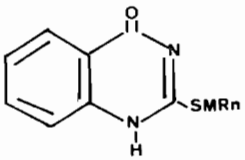
Although the presence of a phenyl ring in H_2TQ might be expected to increase π-charge delocalization relative to H_2Tu and shift the tautomeric equilibrium toward the enol-thioenol form **II**,



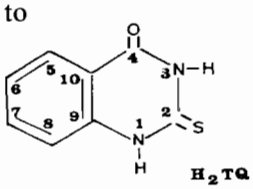
II

this seems not to be the case, at least in the solid state, in which H_2TQ, like H_2Tu, adopts form **I** [1, 2].

Following our studies of the influence of deprotonation and subsequent metallation with organometallic cations on the tautomerism of heterocyclic systems [3], we have now explored the complexation reactions between H_2TQ and R_nM^+ (R = Me or Ph; $n = 1$ (M = Hg) or 2 (M = Tl)). A priori, the 'soft' Lewis acids RHg^+ should promote the evolution of H_2TQ toward the thiol form after the cleavage of the proton from N(3) [4], as has already been observed in RHgHTu [3a].



Subsequent keto-enol displacement should lead finally to



H_2TQ

extending π-charge delocalization.

This rearrangement would be limited by 'harder' Lewis acids such as diorganothallium cations [5], which would not promote complete evolution of the ligand toward the thiol form, or by bimetallation to form $(R_nM)_2TQ$ (at least in organomercury derivatives, since RHg^+ prefers the second metallation site to be a nitrogen atom [6]).

These hypotheses were tested by studying the above mentioned R_nMHTQ and $(R_nM)_2TQ$ compounds in the solid state and in solution, using vibrational and multinuclear NMR spectroscopy.

Experimental

Reagents

2-Thioquinazolinone, MeHgAc and PhHgAc were commercial products. Me_2TlOH and Ph_2TlOH were prepared by treatment of Me_2TlI or Ph_2TlBr with an

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TABLE 1. Analytical data and physical properties of the compounds

Compound	Found (calc.) (%)			Colour	Melting point (°C)
	C	H	N		
MeHgHTQ	27.4 (27.5)	2.0 (2.1)	7.3 (7.1)	white	230
$(MeHg)_2TQ$	19.6 (19.8)	1.5 (1.7)	4.6 (4.6)	white	200
PhHgHTQ	35.2 (36.2)	2.1 (2.1)	6.1 (5.5)	white	230
$(PhHg)_2TQ$	32.2 (32.8)	1.9 (1.9)	3.7 (3.8)	white	210
Me_2TlHTQ	29.0 (29.2)	2.7 (2.7)	6.7 (6.8)	white	220
Ph_2TlHTQ	39.6 (39.3)	2.4 (2.5)	3.2 (3.2)	white	205

aqueous suspension of freshly prepared Ag_2O. Me_2TlI and Ph_2TlBr were obtained as described elsewhere [3b].

Synthesis of compounds

(i) The monoorganomercury(II) compounds were all obtained by the same procedure, described here with reference to the methylmercury(II) derivatives.

MeHgHTQ. A suspension of 0.648 g (3.1 mmol) of H_2TQ in 60 ml of methanol was neutralized with alcoholic NaOH until a clear solution was obtained (pH *c.* 8, direct measurement). This solution was added to 1.000 g (3.6 mmol) of $MeHgOOCCH_3$ suspended in 50 ml of the same solvent. After stirring for 2 days, a white solid was filtered off and dried *in vacuo*. $(MeHg)_2TQ$ was prepared in the same way using 0.389 g (2.2 mmol) of H_2TQ and 1.200 g (4.4 mmol) of $MeHgOOCCH_3$.

For the preparation of phenylmercury(II) complexes $PhHgOOCCH_3$ was used instead of the methylmercury(II) acetate and the reactions were carried out in ethanol.

(ii) For the diorganothallium compounds an aqueous solution of R_2TlOH was slowly added with stirring to a methanolic solution of H_2TQ prepared as in (i). Reactions with both 1:1 and 2:1 mole ratios of reactants gave the monometallated complexes R_2TlHTQ; however, we were unable to obtain the dimetallated derivatives.

Chemical analysis and physical measurements

Analytical data were obtained from Galbraith Lab. Inc., Knoxville, TN (for organomercury(II) compounds) or using a Perkin-Elmer model 250B analyser, and are listed in Table 1. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI and FAB conditions (EI: direct injection, 70 eV, 250 °C; FAB: matrix, 3-nitrobenzyl alcohol (MNBA), Xe, 8 eV). IR spectra were recorded in Nujol mulls, KBr pellets or DMSO solutions on a Perkin-Elmer 180 spectrometer. Raman spectra of powdered samples in capillary tubes were obtained on a Dilor Omars 89 spectrometer (Ar^+ ion laser, 5145 Å). ^1H and ^{13}C NMR spectra in DMSO were recorded at room temperature on a Bruker WM-250 spectrometer at 250.13 and 62.83 MHz, respectively; shifts were measured relative to the solvent signal. ^{205}Tl NMR spectra were recorded at room temperature on a Bruker AM-400 spectrometer at 230.81 MHz, and shifts are relative to external aqueous $TlClO_4$ after extrapolation to infinite dilution. Chemical shifts are given in ppm with positive values to high frequency. Attempts to measure $\delta(^{199}Hg)$ were unsuccessful even when the same experimental conditions and more con-

TABLE 2. Mass spectra (EI and FAB) of RHgHTQ and $(RHg)_2TQ$ derivatives (*m/z* (%))[a]

Ion	MeHgHTQ[b]		PhHgHTQ[c]	$(MeHg)_2TQ$[d]		$(PhHg)_2TQ$[e]
	EI	FAB	EI	EI	FAB	EI
$[M+RHg]$					823(9.2)	
$[M+H]$		395(15.4)				
$[M]$	394(63.0)		456(2.1)	608(2.1)	608(47.6)	
$[(RHg)_2S]$	464(1.5)			464(5.6)		
[RHgSHg]	449(1.0)			449(3.4)		
$[M\text{-}RHg]$				394(43.7)		456(0.5)
$[R_2Hg]$			356(11.4)			356(11.0)
[RHgS]						312(0.3)
[RHg]	217(24.1)		279(6.7)			279(5.8)
[Hg]	202(16.1)		202(42.5)	202(72.5)		202(22.2)

[a]Only ions containing mercury are included. Nominal values calculated using the most abundant isotope ^{202}Hg. [b]Base peak, EI, ligand fraction, *m/z*: 119; FAB, ligand fraction, *m/z*: 136. [c]Base peak, $C_{16}H_8N_4O_2S$, *m/z*: 320. [d]Base peak, EI, ligand fraction, *m/z*: 90; FAB, ligand fraction, *m/z*: 136. [e]Base peak, Ph, *m/z*: 78.

TABLE 3. Mass spectra (EI and FAB) of R_2Tl^+ derivatives (*m/z* (%))[a,b]

Ion	Me_2TlHTQ		Ph_2TlHTQ
	EI	FAB	FAB
$[M+TlR]$			817(1.5)
$[M+Tl]$			741(2.0)
$[M+H]$		413(12.6)	537(14.7)
$[M]$	412(3.3)		
$[M-R]$	397(34.2)	397(5.8)	459(18.1)
$[M-2R]$	382(15.5)		
$[R_2Tl]$	235(34.6)	235(36.4)	
[Tl]	205(100.0)	205(28.2)	205(56.6)

[a]Only ions containing thallium are included. Nominal values calculated using the most abundant isotope ^{205}Tl. [b]Base peak in FAB spectra MNBA, *m/z*: 154.

centrated solutions were used than for 2-thiouracil derivatives [3a].

Results and discussion

Mass spectra

Tables 2 and 3 list the most relevant metallated ions detected in the mass (IE and FAB) spectra. In the monometallated methyl compounds both molecular M^+ (IE spectra) and pseudomolecular $(M+H)^+$ (FAB spectra) ions were observed; in the thallium compound both primary ionization processes occurred (breaking of the metal–ligand bond and demethylation of Tl [5]). As in the case of 2-thiouracil derivatives [3a], the monometallated phenyl compounds were much less stable under electron bombardment: no metallated ions were detected for Ph_2TlHTQ, while $[Hg]^+$ accounted for a large proportion of the ion current in the PhHgHTQ spectrum. As has been reported before [7], FAB-MS seems to be a more adequate tool for the study of these phenyl derivatives.

For $(MeHg)_2TQ$, both the IE and FAB spectra contain the $[M]^+$ peak although its relative abundance is greater in the FAB spectrum. Note the presence in this spectrum of the ion $[M+MeHg]$, which was probably formed by a secondary reaction in the matrix involving the second N atom of the TQ^{2-} ring as an additional metallation centre.

IR spectra

Table 4 lists the positions of the H_2TQ bands that undergo the most significant shifts or disappear upon coordination. For the free ligand, the assignment of these bands was made following refs. 8–10 and bearing in mind the data for complexes with related ligands [3a, 3c].

As Table 4 shows, in the R_nMHTQ complexes ν(N–H) and τ(N–H) remain practically in the same positions as in the free ligand, whereas they disappear in the $(R_nM)_2TQ$ complexes in keeping with the double deprotonation of H_2TQ. The ligand band ν(C=O) shifts to lower wavenumbers in all the compounds, the size

TABLE 4. Most significant ligand IR bands in the free ligand and its complexes

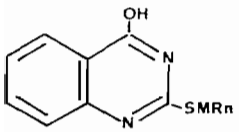
Assignments	H_2TQ	MeHgHTQ	$(MeHg)_2HTQ$	PhHgHTQ	$(PhHg)_2HTQ$	Me_2TlHTQ	Ph_2TlHTQ
ν(NH)	3180sh	3180m		3190m		3190m	3180m
	3080s, b						
ν(C=O)	1705s, b	1675s	1605s	1670m	1620s	1655s	1660m, b
						1635s	
β(NH)[a] + β(CH) + ν(ring)	1630s	1620s	1595s	1610s	1600s	1630s	1620s
	1615s	1610s				1620s	
	1570s	1595s	1580s	1590s	1590s	1600s	1600s
		1570s		1570m	1570m	1580sh	1575m
	1550s	1540s	1500s	1540s	1500s	1520s	1535s
β(CH)	1430vs	1410m	1410m	1405m	1415m	1405m	1415m
β(CH) + ν(ring)	1340m	1335m	1335m	1350m	1350m	1335m	1340m
				1330m	1330s		
	1300s	1300s, b	1310s	1305sh	1320s	1305m	1320m
				1295s			
ν(ring) + β(NH)[a]	1270s	1275m	1270m	1275m	1275	1250s	1270s
		1260m				1240s	
ν(C=S)	1160s	1170s	1160m	1160w	1150w	1160s	1150m
ν(ring)	975m	995m	985m	995m	985m, b	970s	980m
		955m	975m				
τ(NH)	830s	820m		820m		840m	830m
α(ring) + β(CH)	770sh	765s	770sh	765sh	765sh	770s	775m
	760vs	755s	760s	755s	755s	750m	760m

[a]Not in the dimetallated compounds. vs = very strong; s = strong; m = medium; w = weak; sh = shoulder; b = broad.

TABLE 5. ^{1}H and ^{205}Tl NMR spectra of H_2TQ and its complexes[a,b]

Compound	NH	H(5)–H(8)	MR_n	$^{n}J(^{1}H–M)$	^{205}Tl
H_2TQ	12.70s[c](1)[d] 12.50s(1)	7.34–7.94			
MeHgHTQ	12.35s(1)	7.30–7.94	0.80t(3)	192.3	
$(MeHg)_2TQ$		7.24–7.94	0.82t(3)	196.7	
PhHgHTQ	10.03	7.34–7.94	H_o = 7.49d H_m, H_p } 7.28d		
$(PhHg)_2TQ$		7.21–7.95			
Me_2TlHTQ	11.62s(1)	7.15–7.85	0.84d(6)	421.2	3554.01
Ph_2TlHTQ	11.85s(1)	7.21–7.90	H_o = 7.83dd H_m = 7.42dt	450.8 137.1	

[a]Numbering scheme:



[b]In ppm. J values in Hz. [c]s = singlet; d = doublet; dd = doublet of doublets; t = triplet. [d]Relative number of protons from integrated intensities.

of the shift being as in the case of 2-thiouracil derivatives [3a], larger for the dimetallated complexes. As previously discussed [3a], however, these shifts must be used cautiously in diagnosing coordination because this mode is influenced not only by metal coordination, but also by the deprotonation and subsequent partial thione-to-thiol evolution of the ligand.

The bands between 1630 and 1430 cm^{-1} undergo smaller shifts than those of the related thiouracil complexes [3a], probably due to the influence of the adjoining homocyclic ring. The 1550 cm^{-1} band previously attributed to thioamide I [8, 9] undergoes shifts to lower wavenumbers that are larger in the dimetallated complexes, showing the effect of the N-coordination that occurs in these systems.

The intensity of the 1160 cm^{-1} band decreases upon coordination in keeping with its recent assignment as ν(C=S) [10, 11] in related systems.

As has previously been reported for related S,N-coordinated compounds [8, 9, 12] coordination hardly alters the bands at 770 and 760 cm^{-1} in the free ligand. These bands have been intrepreted as due to thioamide IV with a strong contribution from ν(C=S) [8, 9]. However, the non-modification of their intensity and position under S-coordination suggests that they have only a weak ν(C=S) contribution.

To sum up, the changes in the ligand bands upon coordination suggest that the ligand is N,S-coordinated in the dimetallated complexes and S-coordinated, with probably a weak interaction through one of the ring nitrogen atoms, in the monometallated complexes [3a, 13].

With regard to the organometallic fragment vibrations, $\rho(CH_3)$ reinforces the 1160 cm^{-1} band in the MeHgHTQ complex whereas $(MeHg)_2TQ$ has two bands related to this mode (at 1190 and 1165 cm^{-1}) probably due to the presence of both N- and S-bound methylmercury(II) [14]. The N,S-coordination in $(MeHg)_2TQ$ is also supported by its having two bands associated with the ν(Hg–C) mode (at 550 and 535 cm^{-1} in the IR spectrum and 551 and 533 cm^{-1} in the Raman spectrum). Unfortunately, the IR spectrum of MeHgHTQ is very complicated in this region and its Raman spectrum is of very poor quality, so that assignment of these modes was not possible.

In Me_2TlHTQ as in Me_2TlHTu [3a, 13], ν_{asym}(C–Tl–C) (500 cm^{-1} (IR), 500 cm^{-1} (Raman)), is at lower wavenumbers than in other systems [15], whereas ν_{sym}(C–Tl–C) (486 cm^{-1}, Raman) is in a normal position. Like the corresponding 2-thiouracil compounds [3a], the phenyl compounds show bands near 250 cm^{-1} that are attributable to the t mode, although they may have a ligand component. The bands located in the range 250–300 cm^{-1} and about 200 cm^{-1} may also be mixed, the former being contributed to by ligand vibrations and ν(M–S), and the later by ligand vibrations and ν(M–N) [3a and refs. therein].

With regard to the IR spectra in DMSO solution H_2TQ shows a broad band of weak intensity at about 3400 cm^{-1}, indicating a low concentration of the enol

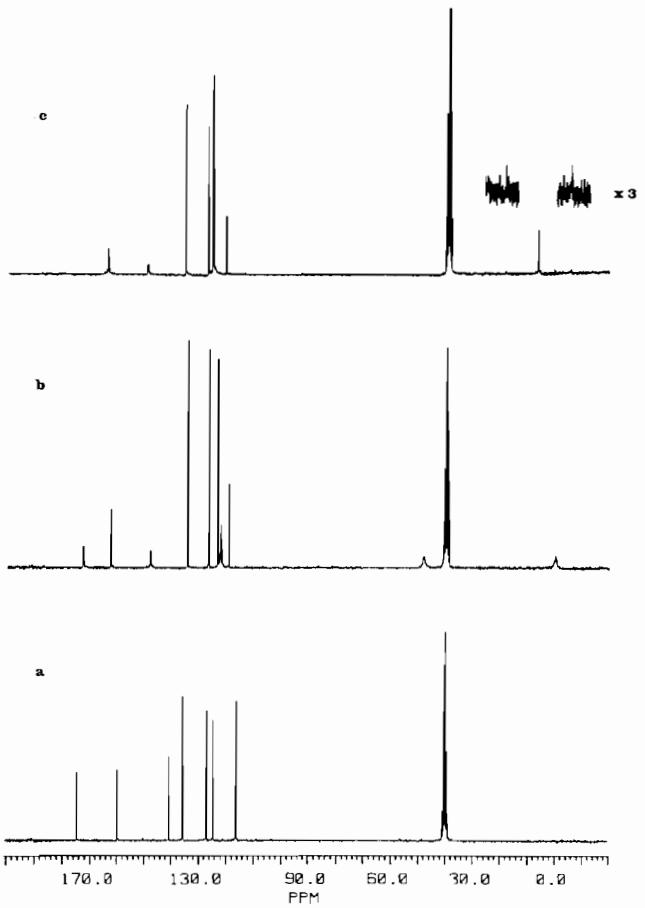


Fig. 1. ^{13}C spectra of H_2TQ (a), $Me_2Tl(HTQ)$ (b) and MeHg(HTQ) (c) (the insert shows the satellite peaks due to ^{13}C–^{199}Hg coupling).

form. The intensity of this band relative to the band about 1700 cm^{-1} increases considerably in MeHgHTQ and PhHgHTQ and rather less in Me_2TlHTQ and Ph_2TlHTQ suggesting a lower ratio of enol forms in the thallium complexes. Comparison of these spectra with those of the 2-thiouracil and related metallated derivatives [3a] shows the 3400 cm^{-1} band to be more intense in the 2-thioquinazolinone compounds showing that the fused phenyl ring of H_2TQ contributes to shift the molecule toward the enol form.

^1H, ^{13}C and ^{205}Tl NMR spectra

Tables 5 and 6 list the chief features of the ^1H and ^{13}C NMR spectra of the ligand and complexes. The ligand spectrum was interpreted taking previous work on 2,4-(1*H*,3*H*) quinazolinediones into account [16, 17]. Because C=S bonds have a greater shielding effect than C=O bonds [18], the two peaks at 174.4 and 159.7 ppm in the ^{13}C NMR spectrum were assigned to C(2) and C(4), respectively. When these values are compared with those found for H_2Tu [3a], only a slight shielding effect due to the fused phenyl ring is observed.

TABLE 6. ^{13}C NMR spectra of H_2TQ and its complexes[a]

Compound	C(2)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	MR_n	$^1J(^{13}C–M)$
H_2TQ	174.4	159.7	126.8	124.3	135.3	115.9	140.5	116.2		
MeHgHTQ	162.3	162.3	126.1	124.5	134.3	124.5	147.8	119.6	7.3	1475.7
$(MeHg)_2TQ$	170.9	165.4	126.3	124.6	133.5	123.9	149.1	121.0	4.5	
PhHgHTQ	162.7	162.7	126.1	124.5	134.3	124.5	148.2	119.7	$C_i = 155.8$ $C_o = 137.1$ $C_m = 128.5$ $C_p = 128.0$	
$(PhHg)_2TQ$	168.8	165.5	126.3	124.6	133.5	123.9	149.2	120.6	$C_i = 153.0$ $C_o = 137.3$ $C_m = 128.5$ $C_p = 128.2$	
Me_2TlHTQ	172.2	162.1	126.1	122.9	133.9	121.9	147.4	118.8	24.0	3018.0
Ph_2TlHTQ	171.5	161.9	126.2	123.3	134.1	122.1	147.2	118.9	125.1 – 207.4	

[a]In ppm. *J* values in Hz. For numbering scheme, see Table 5.

In the ^{1}H NMR spectrum of MeHgHTQ the signals of the two N–H ligand groups become a single signal located at slightly higher field. Its breadth is in keeping with the existence of tautomeric equilibrium. The shift of this band toward lower frequencies is greater in the PhHgHTQ derivative and, as might be expected, the band is not present in $(RHg)_2TQ$. The value of $^{2}J(^{1}H–^{199}Hg)$ for MeHgHTQ suggests thione-to-thiol evolution during the metallation process [19].

The ^{13}C NMR spectra of the ligand and the Me_nMHTQ compounds are shown in Fig. 1. Metallation greatly changes the H_2TQ spectrum, and more for the mercury than for the thallium compound. In the Me_2TlHTQ spectrum, signals for each of the eight ring carbons remain, although some are rather shifted from their position in the spectrum of the free ligand. As in the spectrum of MeHgHTQ two signals disappear some additional work was necessary. The assignments of Table 6 are based on DEPT [20] and proton-coupled experiments, and on spectral behaviour of monoorganomercury(II) complexes of 2-thiouracil [3a]. Only C(6) behaves differently in mercury than in thallium compounds, exhibiting slight deshielding in the former and significant shielding in the latter. In all the monometallated complexes the signals of C(2), C(5) and C(7) are shifted toward lower frequencies, while the peaks of C(4), C(8), C(9) and C(10) shift to high frequencies. Due to the shielding of C(2) as a result of the thione-to-thiol evolution [18], and to the deshielding of C(4), the signals of these two carbons merge, giving a single peak in mercury compounds. The C(6) and C(8) behave similarly, although this time the displacement occurs mainly in just one signal, that of C(8). The slight shift in C(4) upon metallation does not rule out simultaneous keto-to-enol evolution. Even fixed keto groups in heterocycles have highly deshielded signals [21], probably because the canonical forms with the $C^{+}–O^{-}$ charge distribution are important in the free ligand molecule; hence prototropic equilibrium leading to enol forms after metallation should not greatly modify the position of the C(4) signal. One can, however, expect some broadening of the signal if there is equilibrium; the fact that the bandwidth of C(4) in MeHgHTQ, 8 Hz, is reduced to 4 Hz when CF_3COOH is added suggests that this signal is to some extent affected by proton interchange.

Dimetallation strongly deshielded C(2) and, less intensely, C(4), which, as in 2-thiouracil derivatives [3a], is evidence that the second organometallic cation is preferentially bound to the N(3) atom. Interchange between the coordination positions of S- and N-bound RHg groups is fast at room temperature so that the methyl groups of $(MeHg)_2TQ$ afforded just a single signal located between the ranges where the methyl signals of S–HgMe and N–HgMe compounds are usually found [6].

The ^{205}Tl NMR spectrum of Me_2TlHTQ exhibits the multiplicity and intensity ratios expected for a monomer. The value of the ^{205}Tl chemical shift is close to that for the corresponding compound of 2-thiouracil (3527.8 ppm at similar concentration in DMSO) but clearly greater than those of Me_2TlH_2Tb [3b] and Me_2TlH_2Tot [3c].

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