Reaction of dimethylhydroxythallium(III) with 2-thioorotic acid. Crystal structure of dimethyl(2-thioorotato)thallium(III) monohydrate

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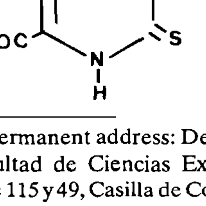
Abstract

Reacting 2-thioorotic acid (H_3Tot) and its monosodium salt with dimethylthallium(III) hydroxide yielded the compounds $TlMe_2H_2Tot \cdot H_2O$ and $(TlMe_2)_2HTot \cdot 2H_2O$, respectively. The monometallated compound crystallizes in the $P2_1/n$ space group with $a = 9.539(4)$, $b = 10.725(3)$, $c = 10.892(3)$ Å, $\beta = 94.55(3)°$ and $Z = 4$. The thallium atom is bonded to the methyl carbons and to one of the oxygens of the carboxylate group of a ligand molecule, and forms further weak bonds with a carbonylic oxygen, a carboxylic oxygen and a thiocarbonylic sulfur of other ligands, as well as with the oxygen of a water molecule. The coordination polyhedron about the thallium atom is a deformed pentagonal bipyramid with the methyl groups in the axial positions. In DMSO solution the compound behaves as a 1:1 electrolyte and the ligand signals of its ^1H and ^{13}C NMR spectra are analogous to those of NaH_2Tot. The coordination characteristics of $(TlMe_2)_2HTot \cdot 2H_2O$ are compared with those of the monometallated compound on the basis of spectroscopic properties in the solid state (IR and Raman) and in solution (^1H and ^{13}C NMR).

Introduction

Like other pyrimidine derivatives, 2-thioorotic acid (H_3Tot) has been tested as a potential antiviral and anticancer agent. It exhibits non-specific activity against certain viral illnesses by stimulating active lymphocyte production [1], and has anti-microbial effects on *E. coli* [2]. It is also an efficient inhibitor of the synthesis of the nucleotide citidine [3] and of thyroid activity [4].

A vibrational study [1] has shown that in the solid state H_3Tot adopts the keto-thione form



but in solution several tautomers may exist [5]. Its ease of deprotonation ($pK_{a1} = 2.27$, $pK_{a2} = 7.90$ [6]) increases its versatility as a ligand. Complexes of the ions H_2Tot^- and $HTot^{2-}$ have been isolated whose ligand–metal bonds have been described, principally on the basis of IR spectroscopy, as variously involving the ligand carboxylate, carbonyl, thiocarbonyl or nitrogen [1, 6, 7].

In this work we studied the reactions of H_3Tot and NaH_2Tot with Me_2TlOH, which afforded the complexes $TlMe_2H_2Tot \cdot H_2O$ and $(TlMe_2)_2HTot \cdot 2H_2O$. In the former case, crystals suitable for X-ray diffraction were obtained and its crystal structure was solved. As far as we know, this is the first X-ray diffraction study involving 2-thioorotic acid. The coordination characteristics of $(TlMe_2)_2HTot \cdot 2H_2O$ were investigated spectroscopically.

Experimental

Elemental analyses (C, H and N) were performed in a Perkin-Elmer 240B elemental analyser. Con-

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ductivity measurements were made using a WTW conductivity meter. IR spectra were recorded on a Perkin-Elmer 180 spectrometer. Raman spectra were obtained on a Dilor Omars 89 spectrometer (Ar^+ ion laser, 5145 Å). ^1H and ^{13}C NMR spectra were recorded at room temperature on a Brucker WM-250 spectrometer at 250.13 and 62.83 MHz, respectively. ^{205}Tl NMR spectra were recorded at room temperature on a Brucker AM-400 spectrometer at 230.81 MHz.

Preparation of $TlMe_2H_2Tot \cdot H_2O$

The ligand (0.472 g, 2.7 mmol) was dissolved in ethanol (75 ml) after partial neutralization with aqueous NaOH. To this solution was added dropwise a solution of $TlMe_2OH$ (aq) (2.7 mmol) prepared as described previously [8]. The mixture was stirred for several hours, and after partial elimination of the solvent under reduced pressure a white crystalline precipitate formed which was filtered off and vacuum dried. m.p. 280 °C. *Anal.* Found: C, 19.6; H, 2.6; N, 6.5. Calc. for $C_7H_{10}N_2O_4STl$: C, 19.72; H, 2.30; N, 6.52%.

Preparation of $(TlMe_2)_2HTot \cdot 2H_2O$

An aqueous solution of dimethylthallium hydroxide [8] (2.7 mmol, 25 ml) was added slowly with stirring to an aqueous solution (25 ml) of 2.7 mmol of the sodium salt of 2-thioorotic acid (prepared by reacting equimolar quantities of 2-thioorotic acid and sodium hydrogen carbonate). After stirring (24 h) and cooling, a crystalline precipitate appeared that was filtered off and vacuum dried. m.p. 250 °C (decomp.) *Anal.* Found: C, 16.6; H, 2.7; N, 4.2. Calc. for $C_9H_{18}N_2O_5STl_2$: C, 16.50; H, 2.76; N, 4.27%.

Crystal structure determination

Crystal data for $TlMe_2H_2Tot \cdot H_2O$

$C_7H_{10}N_2O_4STl$, $M = 422.27$, monoclinic, space group $P2_1/n$, $a = 9.539(4)$, $b = 10.725(3)$, $c = 10.892(3)$ Å, $\beta = 94.55(3)°$, $V = 1116.6$ Å^3, $Z = 4$, $D_c = 2.512$ g cm^{-3}, $F(000) = 780$, λ(Mo Kα) $= 0.71071$ Å, $\mu = 147.85$ cm^{-1}.

Data collection and processing

A colourless 0.08×0.08×0.08 mm crystal was examined at room temperature by $\omega/2\theta$ scan on a CAD4 automated four-circle diffractometer with graphite-monochromated Mo Kα radiation. Of the 2733 reflections recorded to θ_{max} of 25°, 2579 were unique (R_{int} 0.027), of which 1431 with $I > 3\sigma(I)$ were used in refinement after correction for Lorentz and polarization effects and application of an empirical correction factor [9] (minimum and maximum transmission values 0.845–1.228).

Structure analysis and refinement

The structure was solved by the heavy-atom method. After locating the Tl atom with a Patterson map, subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps enabled all the non-hydrogen atoms in the structure to be located. They were assigned anisotropic thermal parameters. Hydrogen atom positions were not calculated. Weighting of the form $w^{-1} = \sigma^2(F_o)$ was used; the agreement factor converged to $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.028$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.031$ and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2} = 3.082$ for 137 variables, where $N_o =$ number of observed reflections and $N_v =$ number of variables. The largest shift/e.s.d. in the final least-squares cycle was 0.18; the maximum residual electron density in the difference Fourier map was 1.072 e Å^{-3} around the Tl atom; secondary extinction coefficient $3.586(2) \times 10^{-7}$ [10]. Neutral scattering factors were used [11]. Calculations were performed on a DEC MicroVAXII computer using SHELX86 [12] and SDP/VAX [13].

Results and discussion

Under the conditions used when H_3Tot was employed, the ligand must be monodeprotonated, leading to synthesis of the monometalled compound in keeping with the stoichiometry actually found. At the pH at which the second synthesis was carried out (pH ≈ 9), the value of pK_{a2} for 2-thioorotic acid [6] means that about 90% of the ligand is present as $HTot^{2-}$, which allows the 2:1 compound to be formed.

Structure of $TlMe_2H_2Tot \cdot H_2O$

The atomic numbering scheme of $TlMe_2H_2Tot \cdot H_2O$ is shown in Fig. 1 [14], and the atomic positions, bond lengths and angles are listed in Tables 1, 2 and 3, respectively.

The thallium–ligand interactions indicated in Fig. 1, though apparently differing greatly in intensity (*vide infra*), give a coordination number of 7 for the metal atom, with a pentagonal bipyramidal geometry in which the methyl groups occupy the axial positions. C–Tl–C is almost linear, with unexceptional Tl–C distances, and the angles between atoms in the equatorial positions are close to the value for a regular pentagonal bipyramid (see Table 3). The distance Tl–O(153) (Table 2), in the middle of the range observed for thallium–oxygen bonds in dimethylthallium(III) compounds (2.36–3.25 Å [15]),

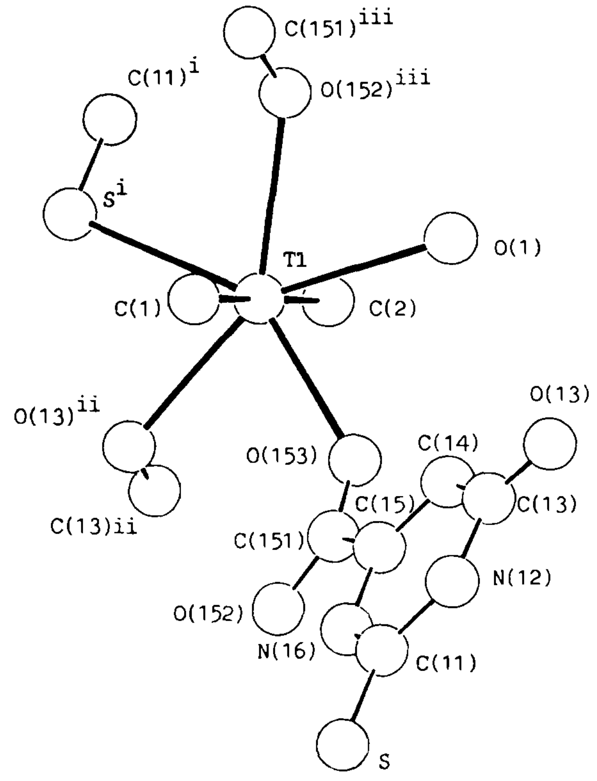


Fig. 1. ORTEP [14] drawing of the compound $TlMe_2H_2Tot \cdot H_2O$ with the atomic numbering scheme and showing the coordination geometry of the thallium atom.

TABLE 1. Positional parameters and their e.s.d.s for $TlMe_2H_2Tot \cdot H_2O$

	x	y	z	U_{eq}^{a}
Tl	0.19892(5)	0.25441(5)	0.08454(5)	0.0154(2)
S	0.2620(4)	0.1010(4)	0.8409(3)	0.024(2)
O(1)	0.034(1)	0.455(1)	0.154(1)	0.023(5)
O(13)	−0.0656(9)	0.3941(8)	0.6249(8)	0.011(4)
O(152)	0.449(1)	0.199(1)	0.4298(9)	0.019(5)
O(153)	0.294(1)	0.316(1)	0.3134(8)	0.022(4)
N(12)	0.094(1)	0.261(1)	0.7146(9)	0.010(4)
N(16)	0.285(1)	0.193(1)	0.6171(9)	0.008(5)
C(1)	0.083(2)	0.113(2)	0.170(2)	0.032(8)
C(2)	0.318(2)	0.399(2)	0.005(2)	0.033(8)
C(11)	0.213(1)	0.189(1)	0.720(1)	0.010(6)
C(13)	0.044(1)	0.336(1)	0.617(1)	0.011(6)
C(14)	0.124(1)	0.335(1)	0.512(1)	0.013(6)
C(15)	0.241(1)	0.265(1)	0.516(1)	0.008(5)
C(151)	0.336(1)	0.261(1)	0.408(1)	0.016(6)

$^{a}U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

TABLE 2. Interatomic distances (Å) in $TlMe_2H_2Tot \cdot H_2O$ and their e.s.d.s

Tl–S^{i}	3.220(4)
Tl–O(1)	2.81(2)
Tl–O(13)^{ii}	2.770(9)
Tl–O(152)^{iii}	2.86(1)
Tl–O(153)	2.668(9)
Tl–C(1)	2.15(2)
Tl–C(2)	2.15(2)
S^{i}–C(11)^{i}	1.65(1)
O(13)^{ii}–C(13)^{ii}	1.23(2)
O(152)–C(151)	1.28(2)
O(153)–C(151)	1.23(2)
N(12)–C(11)	1.38(2)
N(12)–C(13)	1.39(2)
N(16)–C(11)	1.37(2)
N(16)–C(15)	1.38(2)
C(13)–C(14)	1.43(2)
C(14)–C(15)	1.35(2)
C(15)–C(151)	1.54(2)

Symmetry code: (i) $x, y, z-1$; (ii) $0.5+x, 0.5-y, z-0.5$; (iii) $x-0.5, 0.5-y, z-0.5$.

suggests a relatively strong oxygen–metal interaction. The remaining thallium–oxygen distances are all greater and possibly indicative of weak interactions.

The distance Tl–S lies at the upper limit of the range observed in dimethylthallium(III) complexes (2.63–3.35 Å) [15]. Consequently, although this distance is less than the sum of the van der Waals radii (3.76 Å [16]), Tl–S too must be a weak interaction.

To sum up, the thallium atom binds strongly to the methyl carbons and one of the oxygens of a ligand carboxylate group, and weakly to a carbonyl oxygen, a carboxyl oxygen and a thiocarbonyl sulfur of three other ligands, and to the oxygen of the water molecule that forms part of the complex (these relationships are shown in Fig. 2, in which for clarity the SCHAKAL [17] plot has been used instead of the usual ORTEP plot [14] because of the rather complicated lattice packing).

The pyrimidine ring of the ligand is almost planar ($\chi^2 = 0.5$) and forms a dihedral angle of $5 \pm 3°$ with the plane of the carboxylate group. In principle, this would allow delocalization of charge between the two groups of atoms, although the distance C(15)–C(151) (Table 2) does not suggest a multiple bond [18]. The C–O bond lengths in the –COO group are different (even taking the high e.s.d.s into account), the shorter being that of the oxygen that interacts most strongly with the thallium.

The modification of C=O and C=S by interaction with thallium cannot be estimated directly because structural data for H_3Tot are not available. The known structure of 2-thiouracil (H_2Tu) [19] nevertheless allows indirect inference, since H_2Tot^- is effectively a molecule of H_2Tu with a carboxylate group substituted for H(6); if conjugation between the $-COO^-$ group and the pyrimidine ring is weak, as seems to be the case, H_2Tot^- and H_2Tu should be similar as regards their intraannular moiety and

TABLE 3. Bond angles (°) in $TlMe_2H_2Tot \cdot H_2O$ and their e.s.d.s

S^{i}–Tl–O(1)	139.5(2)
S^{i}–Tl–O(13)^{ii}	68.5(2)
S^{i}–Tl–O(152)^{iii}	78.9(2)
S^{i}–Tl–O(153)	145.5(2)
S^{i}–Tl–C(1)	97.7(5)
S^{i}–Tl–C(2)	83.9(5)
O(1)–Tl–O(13)^{ii}	150.1(3)
O(1)–Tl–O(152)^{iii}	64.0(3)
O(1)–Tl–O(153)	73.4(4)
O(1)–Tl–C(1)	95.8(6)
O(1)–Tl–C(2)	83.5(5)
O(13)^{ii}–Tl–O(152)^{iii}	145.9(3)
O(13)^{ii}–Tl–O(153)	77.4(3)
O(13)^{ii}–Tl–C(1)	88.3(5)
O(13)^{ii}–Tl–C(2)	91.5(5)
O(152)^{iii}–Tl–O(153)	135.5(4)
O(152)^{iii}–Tl–C(1)	86.6(5)
O(152)^{iii}–Tl–C(2)	94.8(5)
O(153)–Tl–C(1)	85.5(5)
O(153)–Tl–C(2)	92.8(5)
C(1)–Tl–C(2)	178.2(6)
C(11)–N(12)–C(13)	127(2)
C(11)–N(16)–C(15)	122(2)
S–C(11)–N(12)	123(1)
S–C(11)–N(16)	123(1)
N(12)–C(11)–N(16)	115(2)
O(13)–C(13)–N(12)	119(1)
O(13)–C(13)–C(14)	125(1)
N(12)–C(13)–C(14)	115(1)
C(13)–C(14)–C(15)	119(1)
N(16)–C(15)–C(14)	122(1)
N(16)–C(15)–C(151)	115(2)
C(14)–C(15)–C(151)	122(2)
O(152)–C(151)–O(153)	128(1)
O(152)–C(151)–C(15)	115(2)
O(153)–C(151)–C(15)	117(1)

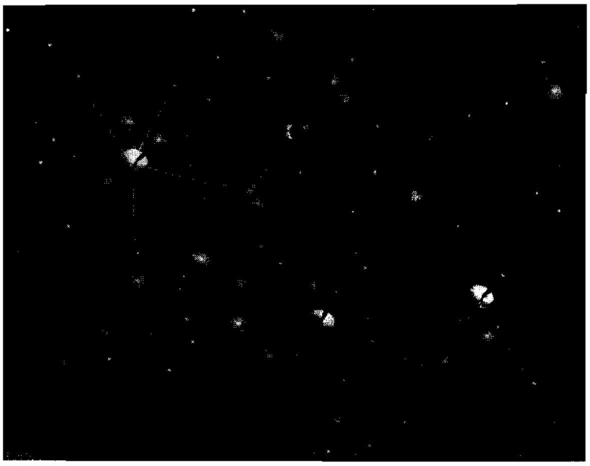
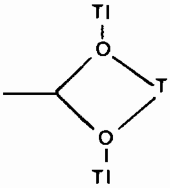


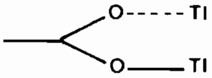
Fig. 2. SCHAKAL [17] plot of the lattice of the compound $TlMe_2H_2Tot \cdot H_2O$.

carbonyl and thiocarbonyl groups. Comparing bond distances and angles for H_2Tu [19] and $TlMe_2H_2Tot \cdot H_2O$ (Tables 2 and 3) reveals small but significant differences for certain distances (e.g. N(16)–C(11)), probably due to the difference in strength between the H_2Tu hydrogen bond [19] and the Tl··O=C and Tl··S=C interactions in $TlMe_2H_2Tot \cdot H_2O$. Note that although the structure of $TlMe_2HTu$ [20] is known, it is not comparable with those of $TlMe_2H_2Tot \cdot H_2O$ because the lack of the N(16)–H proton in its 2-thiouracilate anion must strongly affect the distribution of charge in the pyrimidine ring and in the *endo-* and *exo*-annular bonds, making it difficult to establish which changes in these bonds arise from deprotonation of the ring and which from interaction with thallium. $TlMe_2HTu$ seems likely to be similar to $(TlMe_2)_2HTot \cdot 2H_2O$.

Finally, it is worth noting that, although what appears to be the strongest bond between the ligand and the organometallic cation involves the carboxylate group, the situation is very different from that of dimethylthallium(III) acetate [21], in which the $-COO^-$ group is both chelating and bridging



In $TlMe_2H_2Tot \cdot H_2O$ it forms an asymmetric bridge



The coordination of the metal is also different.

IR spectra

Table 4 lists the spectral data for the most interesting bands of the sodium salt of the ligand [1] and its complexes. Only the band at 3520 cm^{-1} is specific to the coordinated water of $TlMe_2H_2Tot \cdot H_2O$, since the presumable water vibrations at about 1600 and 850 cm^{-1} reinforce ligand bands located in these regions [1]. The location of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in virtually the same position in the sodium salt of the ligand and in $TlMe_2H_2Tot \cdot H_2O$ is in keeping [22] with the carboxylate group's acting as a bridging group in the latter. The interaction of the C=O and C=S groups with Me_2Tl^+ does not alter the spectrum significantly: ν(C=O) and the bands at 1030 and 940 cm^{-1}, both of which have a ν(C=S) component [1], all have virtually the same positions and intensities in the sodium salt and the Me_2Tl^+ complex, the intensity of the band at 1230 cm^{-1} is slightly modified, and at 1210 cm^{-1} there appears a shoulder that has been

TABLE 4. Most significant bands (cm^{-1}) in the IR spectra of the sodium salt of the ligand and its complexes

Compound	ν(OH)	ν_{as}(COO$^-$)	ν_s(COO$^-$)	ν(C=O)	ν(C=S)	δ(CH$_3$)	ν_{as}(C–Tl–C)
NaH_2Tot		1690s, b	1390s	1650s, b	1030m, 940m		
$TlMe_2H_2Tot \cdot H_2O$	3520m	1680s, b	1385s	1655s, b	1030m, 930m	1170s	545m
$(TlMe_2)_2HTot \cdot 2H_2O$	3440b	1670sh	1400s	1640s, b	1005m, 955m	1180s	550m

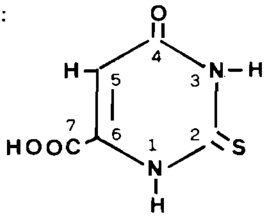
s = strong, m = medium, b = broad, sh = shoulder.

TABLE 5. ^{1}H, ^{13}C and ^{205}Tl NMR parameters for 2-thioorotic acid and complexes[a, b]

Compound	NH	H_5	MRn	$^2J(^1H–^{205}Tl)$
H_3Tot	11.90(s)[c] (1)[d]; 12.69(s)(1)	6.26(s)(1)		
NaH_2Tot	12.39(vb)	5.99(s)(1)		
$TlMe_2H_2Tot \cdot H_2O$	12.35(vb)	6.03(s)(1)	0.87(d)	−441.5
$(TlMe_2)_2HTot \cdot 2H_2O$	11.62(b)	6.05(s)(1)	0.81(d)	−421.8

Compound	C_2	C_4	C_5	C_6	C_7	MRn	$^1J(^{13}C–^{205}Tl)$	^{205}Tl
H_3Tot	176.2	161.3	107.5	142.9	161.2			
NaH_2Tot	174.7	159.6[e]	102.9	149.4	162.8			
$TlMe_2H_2Tot \cdot H_2O$	175.1	161.5[e]	104.0	148.9	162.6	25.2	2914.2	3446.3[f]
$(TlMe_2)_2HTot \cdot 2H_2O$	176.4	168.3[e]	105.1	154.6	164.8	22.6	2922.1	

[a] H_3Tot:



[b] In DMSO-d$_6$ or DMSO/DMSO-d$_6$, δ in ppm referred to the solvent signal in ^{1}H and ^{13}C NMR spectra and referred to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution in ^{205}Tl spectrum. Values of J in Hz. [c] b = broad, vb = very broad, s = singlet, d = doublet. [d] Number of protons from integrated intensities. [e] Assignments of C_4 and C_7 can be interchanged. [f] 0.016 M solution.

attributed to ν(C=S) in related systems [23]. Of the bands due to vibrations of the organometallic fragment, δ(CH$_3$) is close to its position for other Me_2Tl^+ complexes [24], while ν(C–Tl–C) lies near its location for Me_2Tl^+ in solution and in compounds with weak covalent metal–ligand interaction [25].

The broad band at 3400 cm^{-1} in the IR spectrum of $(TlMe_2)_2HTot \cdot 2H_2O$ is due to water. The positions of ν_{as}(COO$^-$), ν_s(COO$^-$) and ν(C=O) appear to indicate that the coordination of the carboxylate and carbonyl groups to the metal is similar to that found in $TlMe_2H_2Tot \cdot H_2O$. The positions of the bands associated with the C=S group suggest that the sulfur atom too coordinates to the thallium atom (Table 4). Furthermore, the NaH_2Tot band at 1550 cm^{-1} shifts to 1510 cm^{-1} and the 720 cm^{-1} band disappears, suggesting deprotonation of the N–H group and coordination of N to the metal atom. Hence the second Me_2Tl^+ group seems to be coordinated to N and S, so that all the ligand donor groups except the undeprotonated N–H group are used. The different coordination sites for the two cations in this compound do not give rise to the splitting of ν_{as}(C–Tl–C) (Table 4) or ν_s(C–Tl–C) (a strong Raman band at 496.5 cm^{-1}). However, the participation of the S and N atoms in coordination slightly shifts ν_{as} and ν_s from their positions in $TlMe_2HTot \cdot H_2O$ (ν_s, 490 cm^{-1}, s, Raman).

Studies in solution

Both compounds are soluble in DMSO and DMF. The monometal derivative is sparingly soluble in water. Its conductivity in dimethyl sulfoxide (45 ohm^{-1} cm^2 mol^{-1}) is at the upper limit of the normal range for a 1:1 electrolyte [26] and is possibly due in part to the presence of water in its structure.

Significant ^{1}H and ^{13}C NMR signals are listed in Table 5 alongside those of NaH_2Tot and H_2Tu [24] for comparison. Signal assignment was based on published data [5], the positions of the peaks and

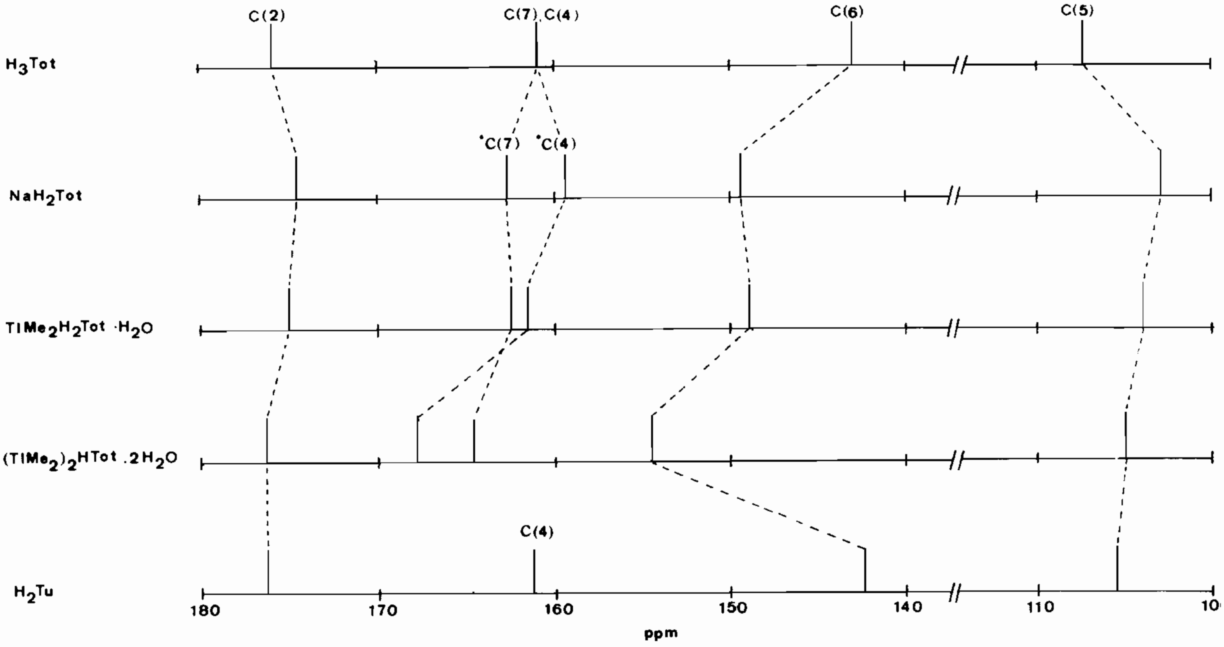


Fig. 3. Chemical shifts in the ^{13}C NMR spectra of 2-thioorotic acid and its derivatives (2-thiouracil [24] is included for comparative purposes). *Signals of C_4 and C_7 can be interchanged.

the splitting of signals in the proton coupled ^{13}C spectrum. The C(4) and C(7) signals could not be differentiated.

A ^{13}C NMR correlation diagram is shown in Fig. 3. The signals of $TlMe_2H_2Tot \cdot H_2O$ and NaH_2Tot are in very similar positions, the greatest difference occurring for the C(4) signal, which in the dimethylthallium complex is more deshielded (1.9 ppm) than in the sodium salt. The general similarity confirms the salt character of $TlMe_2H_2Tot \cdot H_2O$, while the deshielding of the carbonyl carbon appears to suggest weak interaction via this group. The spectrum of H_2Tu confirms its similarity to H_2Tot^-: the only carbon for which the H_2Tu spectrum differs notably from those of the H_2Tot^- derivatives is C(6), which bears a hydrogen atom in H_2Tu and a carboxylate group in H_2Tot^-.

The ^1H NMR spectra are in agreement with the above discussion, as are the ^2J(Tl–H) and ^1J(Tl–C) coupling constants of the organometallic cation, whose values are very close to those observed in DMSO-d_6 for dimethylthallium nitrate and perchlorate [27].

The conductivity of $(TlMe_2)_2HTot \cdot 2H_2O$ (21.7 ohm^{-1} cm^2 mol^{-1}) is much less than that of $TlMe_2H_2Tot \cdot H_2O$, and would seem to exclude its being a 2:1 electrolyte. Its spectral behaviour is also different (Table 5). All the ligand carbons are deshielded with respect to the monometallated compound, with the strongest deshielding occurring for C(6), C(7) and C(4). The modification undergone by the C(7) signal indicates a significant change in the carboxylate group, while the deshielding of C(6) and C(4) follows the pattern observed when H_2Tu forms $TlMe_2HTu$ [24]. The organometallic signals are also different in the monometallated and dimetallated derivatives: the ^1H and ^{13}C chemical shifts of the methyl group are smaller in the latter, ^2J(Tl–H) is less negative and ^1J(Tl–C) is more positive. These observations seem to suggest that the second deprotonation of thioorotic acid allows effective coordination to the dimethylthallium(III) cations,in contrast to the saline character of the monometallated compound. Finally, the absence of different signals for the two $TlMe_2$ groups of $(TlMe_2)_2HTot \cdot 2H_2O$ must reflect rapid interchange of their positions.

Supplementary material

Observed and calculated structure factors are available from author A.C.

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References

1 G. S. Pandey, P. C. Nigam and U. Agarwala, *J. Inorg. Nucl. Chem.*, *39* (1977) 1877.

2 J. Gut, J. Moravek, C. Parkany, M. Prystas, J. Skoda and F. Sorm, *Collect. Czech. Chem. Commun.*, *24* (1959) 3154.

3 K. V. Chelbovz, E. Golovinski and A. A. Hadjiolov, *Biochem. Pharmacol.*, *19* (1970) 2785.

4 C. Halvor, *J. Biol. Chem.*, *162* (1946) 27.

5 M. V. Javanovic and E. R. Biehl, *J. Heterocycl. Chem.*, *24* (1987) 191.

6 N. K. Davidenko and N. N. Zinich, *Koord. Khim.*, *5* (1979) 3.

7 F. Capitán, M. Román and A. Arrebola, *Inf. Quim. Anal.*, *25* (1971) 111; *26* (1972) 135; G. S. Pandey, G. C. Pandey, P. C. Nigam and U. Agarwala, *Indian J. Chem., Sect. A*, *14* (1976) 884; G. S. Pandey, P. C. Nigam and U. Agarwala, *Indian J. Chem., Sect. A*, *15* (1977) 537; G. S. Pandey, P. C. Nigam and U. Agarwala, *Indian J. Chem., Sect. A*, *17* (1979) 74; M. Shrivastava and G. S. Pandey, *Indian J. Chem., Sect. A*, *27* (1988) 477.

8 M. V. Castaño, A. Sánchez, J. S. Casas, J. Sordo, J. L. Brianso, J. F. Piniella, X. Solans, G. Germain, T. Debaerdemaeker and J. Glaser, *Organometallics*, *7* (1988) 1897.

9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, *39* (1983) 158.

10 W. H. Zachariasen, *Acta Crystallogr.*, *16* (1963) 1139.

11 *International Tables for X-ray Crystallography*, Vol. IV. Kynoch Press, Birmingham, U.K., 1976. (Present distributor: Kluwer, Dordrecht, The Netherlands.)

12 G. M. Sheldrick, *SHELX86*, University of Göttingen, F.R.G., 1986.

13 B. A. Frenz & Associates and Enraf-Nonius, *SDP/VAX*, Version 3.0, Delft, The Netherlands, 1986.

14 C. K. Johnson, *ORTEPII, Rep. ORNL-5138*, Oak Ridge National Laboratory, TN, U.S.A., 1976.

15 M. V. Castaño, A. Macias, A. Castiñeiras, A. S. González, E. G. Martínez, J. S. Casas, J. Sordo, W. Hiller and E. E. Castellano, *J. Chem. Soc., Dalton Trans.*, (1990) 1001.

16 A. Bondi, *J. Phys. Chem.*, *68* (1964) 441.

17 E. Keller, *SCHAKAL*, A FORTRAN program for the graphic representation of molecules and crystallographic models, Universität Freiburg, Freiburg, F.R.G., 1986.

18 K. Henrick, R. W. Matthews and P. A. Tasker, *Acta Crystallogr., Sect. B*, *34* (1978) 1347.

19 E. R. T. Tiekink, *Z. Kristallogr.*, *187* (1989) 79.

20 M. S. García Tasende, M. I. Suárez, A. Sánchez, J. S. Casas, J. Sordo, E. E. Castellano and Y. P. Mascarenhas, *Inorg. Chem.*, *26* (1987) 3819.

21 Y. M. Chown and D. Britton, *Acta Crystallogr., Sect. B*, *31* (1975) 1929.

22 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 4th edn., 1986, p. 321.

23 R. A. Yadav, P. N. S. Yadav and J. S. Yadav, *Proc. Indian Acad. Sci. (Chem. Sci.)*, *100* (1988) 69.

24 M. S. García Tasende, M. I. Suárez Gimeno, A. Sánchez, J. S. Casas, J. Sordo and E. E. Castellano, *J. Organomet. Chem.*, *384* (1990) 19.

25 G. D. Shier and R. S. Drago, *J. Organomet. Chem.*, *5* (1966) 330.

26 P. G. Sears, G. R. Lester and L. R. Dawson, *J. Phys. Chem.*, *60* (1956) 1433.

27 J. F. Hinton, K. R. Metz and R. W. Briggs, *Prog. NMR Spectrosc.*, *20* (1988) 423; F. Brady, R. W. Matthews, M. M. Thakur and D. G. Gillies, *J. Organomet. Chem.*, *252* (1983) 1.