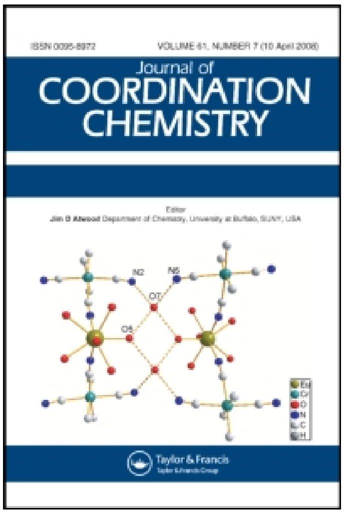


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Investigation of Dimethylthallium(III) Complex Equilibria with 2-Thioorotate by Means of Potentiometric Techniques

M. S. García-Tasende[a]; M. García Bugarín[a]; M. Filella[b]
[a] Departamento de Quimica Inorgánica, Universidad de Santiago de Compostela, Santiago de Compostela, Spain [b] Département de Chimie Minérale, Analylique el Appliquée, Université de Genève, Geneve, Switzerland

To cite this Article García-Tasende, M. S. , Bugarín, M. García and Filella, M.(1992) 'Investigation of Dimethylthallium(III) Complex Equilibria with 2-Thioorotate by Means of Potentiometric Techniques', Journal of Coordination Chemistry, 25: 1, 63 — 73
To link to this Article: DOI: 10.1080/00958979209407903
URL: http://dx.doi.org/10.1080/00958979209407903

J. Coord. Chem. 1992, Vol. 25, pp. 63–73
Reprints available directly from the publisher
Photocopying permitted by license only

INVESTIGATION OF DIMETHYLTHALLIUM(III) COMPLEX EQUILIBRIA WITH 2-THIOOROTATE BY MEANS OF POTENTIOMETRIC TECHNIQUES

M. S. GARCÍA-TASENDE, M. GARCÍA BUGARÍN

Departamento de Química Inorgânica, Universidad de Santiago de Compostela, 15076 Santiago de Compostela, Spain

and M. FILELLA*

Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, Quai Ernest Ansermet 30, 1211 Genève 4, Switzerland

(Received February 22, 1991)

The system comprising dimethylthallium(III), 2-thioorotate (TOA) and hydrogen ions in aqueous solution at 20°C and I = 100 mmol dm^{-3} (nitrate) has been characterized by means of glass-electrode potentiometry. Protonation constants for 2-thioorotate and formation constants for the complexes $[(Me_2Tl)(TOA)]^-$, $[(Me_2Tl)(TOAH_{-1})]^{2-}$ and $[(Me_2Tl)_2(TOAH_{-1})]^-$ are reported.

Keywords: Dimethylthallium(III), 2-thioorotic acid, complexes, stability constants

INTRODUCTION

The utmost importance of understanding biologically mediated transformations yielding organometallic compounds with high potentials for bioaccumulation and toxicity has been demonstrated in the case of methylmercury pollution. Consequently, toxic elements that form organometallic compounds, particularly metal-alkyls, should receive considerable attention.[1,2]

Thallium can form alkyl compounds and the similarity of the organic chemistry of thallium to that of mercury and lead, plus the known toxicity of thallous salts, would suggest that organothallium compounds should be quite toxic.[3] Surprisingly, the little information available on the biological effects of these compounds seems to indicate the contrary; methylthallium compounds are found to be less toxic to bacteria than Tl^+.[4] A number of *in vitro* model experiments concerning methylation of thallium have been carried out. They show that methylcobalamin is not demethylated by Tl(I),[5] yet it is demethylated by Tl(III).[5,6] In the literature only one paper has appeared on the biomethylation of Tl^+;[7] incubation of Tl(I) acetate with anaerobic sediment bacteria from a lake in the absence of light and air yielded small amounts of Me_2Tl^+. However, no work with real sediments has been reported and there is no firm evidence of environmental thallium methylation.[8] Confirmation that Tl^+ is biomethylated to Me_2Tl^+ would be very interesting because it would show that "oxidative methylation" is not unique to Pb^{2+}. The reason why Me_2Tl^+ is less

---

* Author for correspondence.

toxic than Tl^+, while Me_4Pb is much more toxic to bacterial cultures than Pb(II) compounds is not well understood. In the case of thallium, biomethylation could be a pathway for metal detoxification.

Dimethylthallium is the only methylated species stable in aqueous solution. Monomethyl compounds are unstable and tend to decompose in solution[9] and trimethylthallium decomposes instantaneously in water to form Me_2Tl^+ and methane.[10] Relatively little is known of the coordination chemistry of dimethylthallium(III) in solution. Only one reference could be found in the literature, concerning equilibria with β-diketones.[11] Because the behaviour of dimethylthallium(III) may be related to its binding properties, we have undertaken a study of its coordination chemistry in solution with ligands showing various binding strengths. The present paper reports the potentiometric determination of formation constants of dimethylthallium(III)-2-thioorotic acid complexes. This work is a continuation of previous investigations of the complexation of dimethylthallium(III) with sulphur-containing aminoacids[12] and with 2-thiobarbituric acid[13] where some general patterns regarding the complexing behaviour of this organometallic cation in solution were outlined.

EXPERIMENTAL

Materials

Potentiometric assay of 2-thioorotic acid (Aldrich) revealed that no further purification was required. Solutions of thioorotic acid were freshly prepared for each titration by direct weighing. Its poor water solubility (concentrations greater than 5.0 mmol dm^{-3} could not be prepared) limited the use of a wide range of ligand concentrations.

Dimethylthallium(III) nitrate was obtained by neutralizing a solution of dimethylthallium(III) hydroxide (prepared by treating the iodide with silver oxide[14]) with nitric acid.[15] Stock solutions of dimethylthallium(III) were prepared with dilute nitric acid (Merck) to prevent the hydrolysis of the organometallic cation and absorption of carbon dioxide. Their mineral acid contents were determined by Gran plot[16] titrations with standard alkali.

Carbonate-free potassium hydroxide solutions were prepared by diluting Carlo Erba standard volumetric solutions. Alkali titre and absence of carbonate were periodically checked by means of the appropriate Gran plots[16] using potassium phthalate (Merck). Nitric acid solutions were prepared from concentrated acid (Carlo Erba) and were standardized against potassium hydroxide solutions.

All solutions were prepared using demineralized water (Millipore system), boiled and cooled under nitrogen. The ionic strength of the solutions was adjusted to a nitrate concentration of 100 mmol dm^{-3} by the addition of potassium nitrate (Merck).

High-quality nitrogen was scrubbed through sodium hydroxide, pyrogallol, and ionic background solutions thermostatted at 20°C. All solutions were thoroughly flushed with nitrogen before use.

Experimental procedure

Formation constants were determined by performing potentiometric titrations in a double-walled vessel kept at 20 ± 0.05°C and under an atmosphere of purified nitrogen.

The free hydrogen ion concentration was measured with a Radiometer PHM84 pH meter equipped with a wide-range glass electrode (Radiometer G202B) and a calomel reference electrode (Radiometer K401). The electrode system was calibrated in terms of hydrogen ion concentration by performing strong acid *versus* strong base titrations.[17] The autoprotolysis constant of the medium under the experimental conditions used was found to be $10^{-13.88}$.

Working solutions containing ligand, metal (when appropriate) and nitric acid were titrated by adding potassium hydroxide from a Metrohm MultiDosimat 645 autoburette. Initial solutions containing the metal and the ligand were acidified so that all the ligand donor groups were significantly protonated prior to the titration. Metal complex formation curves were obtained at different ligand to metal ratios and for different total ligand and total metal concentrations. The data used in calculating the formation constants are summarized in Table I.

TABLE I

Summary of titration data used in obtaining formation constants. Number of titration points, initial total concentrations of dimethylthallium(III) ($C_{Me_2Tl^+}$), 2-thioorotate (C_{TOA}), and nitric acid (C_H), and the $-\log[H]$ range are given. For the TOA-H$^+$ system, the entire range investigated is shown in brackets. All concentrations are expressed in mmol dm^{-3}.

System	Titration	N. of points	$C_{Me_2Tl^+}$	C_{TOA}	C_H	$-\log[H]$ range
TOA-H$^+$	1	29(46)		2.000	10.050	1.93–9.76(12.17)
	2	25(37)		2.500	2.510	2.31–9.82(12.15)
	3	22(37)		2.500	5.025	3.34–9.85(12.18)
	4	23(38)		2.500	10.050	1.91–9.28(12.16)
Me_2Tl^+-TOA-H$^+$	1	39	0.500	1.000	5.025	3.13–11.74
	2	41	4.000	1.000	5.025	3.03–11.19
	3	48	1.000	2.000	5.025	3.15–11.77
	4	35	2.000	2.000	10.050	3.02–10.95
	5	37	4.000	2.000	10.050	3.13–11.71
	6	50	8.000	2.000	10.050	3.31–11.31

Data treatment

Metal M$^+$, ligand L^{2-} (*i.e.*, deprotonated 2-thioorotic acid, TOA) and H$^+$ ions were chosen as components in evaluating the stability constants. The general three-component equilibria can be written as shown below.

$$\mathrm{p\,M + q\,L + r\,H \rightleftharpoons M_pL_qH_r}$$

Charges are omitted for simplicity. The associated overall formation constant is denoted by β_{pqr}.

Metal hydrolysis formation constant values cited in the literature[18] for the main hydrolysis products of dimethylthallium(III), $Me_2Tl(OH)$ and $(Me_2Tl(OH))_2$, were used. Calculations including the hydroxo complexes showed that metal hydrolysis was negligible under the conditions chosen.

Protonation constants of 2-thioorotate and formation constants of the complexes formed with dimethylthallium(III) were calculated using the latest version of the computer program library ESTA.[19-22] Titration data were treated using the same approach as reported previously,[23-25] *i.e.*, optimization and simulation in successive steps.

Initial tentative identification of the species present was based on the shapes of the experimental protonation and formation curves. Protonation curves represent the average number of protons bound to each ligand, $\bar{r}$, as a function of $-\log[H]$, (*1*),

$$\bar{r} = (C_H + n.C_L - C_{OH} + [OH] - [H])/C_L \qquad (1)$$

where C_H and C_L are the total concentration of strong acid and ligand, respectively, C_{OH} is the total concentration of hydroxide added at a given experimental point, and n is the number of dissociable protons of the ligand. Formation curves express the average number of ligands bound per mol of metal ion, $\bar{p}$, as a function of the free ligand concentration, (*2*),

$$\bar{p} = (C_L - \sum_{0}^{n}[LH_n])/C_M \qquad (2)$$

where C_M is the total metal concentration. The shape of the formation curves was used to deduce the possible stoichiometries of the complex species present in each system as well as to obtain rough estimates for their formation constants. These estimates were consequently introduced into the optimization module of the computer library ESTA as input data and refined.

The final selection of species was based on numerical criteria (lowest sum of squared residuals, R factors) and graphical comparisons between the experimental curves and theoretical ones as simulated using different models. It was verified that all the proposed species existed in significant concentrations over a reasonable range of data.

The ESTA objective function can be minimized with respect to either emf or total ion concentration. The objective functions quoted in Table II are based on unweighted total ion concentration residuals (OBJT) and on weighted emf residuals (OBJE). The weighting scheme proposed by May and Murray was applied throughout the OBJE calculations.[21] The weight at each titration point was based on errors of 0.2% in analytical concentrations, 0.01 cm^3 in titre and 0.1 mV in emf.

Computations were carried out on a VAX 8700 computer and on a COMPAQ DESKPRO 386/20e microcomputer.

RESULTS AND DISCUSSION

The values calculated for the formation constants are shown in Table II.

The TOA–H system

TOA protonation curves revealed two separate buffer zones. Unfortunately, the experimental data obtained only cover a small portion of the rise corresponding to the second stepwise protonation constant (the highest $\bar{r}$ value was 1.12) because of the acidic value of the constant which lies outside the reliable range of response of the glass electrode. Therefore, the value given for the second protonation constant in Table II must be considered as being only a rough approximation. Only about 20% of the experimental points, covering 10% of the rise, contained information allowing calculation.

TABLE II
Formation constants determined in this study at 20°C for $I = 100\,\mathrm{mmol\,dm^{-3}}\ \mathrm{NO_3^-}$ ($\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$).

System		p q r	$\log\beta_{pqr}$	s.d.[a]	O.F.[b]	R[c]	n[d]
TOA-H$^+$	OBJE	0 1 1	7.830	0.003	0.21	0.002	99
		0 1 2	8.828[e]	0.030			
	OBJT	0 1 1	7.831	0.003	$4.68.10^{-10}$	0.006	99
		0 1 2	8.844[e]	0.015			
Me$_2$Tl$^+$-TOA-H$^+$	OBJE	1 1 0	2.239	0.010	0.38	0.002	250
		1 1-1	−8.294	0.010			
		2 1-1	−5.942	0.019			
	OBJT	1 1 0	2.240	0.011	$8.21.10^{-10}$	0.015	250
		1 1-1	−8.291	0.009			
		2 1-1	−5.941	0.019			

[a] Standard deviations given by the programs.

[b] O.F., in OBJE output $= [\sum w(\mathrm{emf}_i^o - \mathrm{emf}_i^c)^2]/(N\text{-}n_p)$; in OBJT output $= [\sum w(T_i^o - T_i^c)^2]/(N\text{-}n_p)$, where N = no. of points, n_p = no. of refined parameters, T_i = total concentrations.

[c] R = Hamilton R factor.

[d] Number of points used in the calculations.

[e] Approximate value. The standard deviation quoted does not reflect the poor reliability of the calculated value (see text).

2-Thioorotic acid has a third proton that may be released at higher −log[H] values, the ligand being a potential triprotic acid. Titrations were continued to −log[H] = 12 (Table I); a plateau was obtained from 10 to 11 and the electrodes gave an erratic response at values of −log[H] higher than 11 and the curves were no longer reproducible. Therefore, 2-thioorotic acid is considered as being a diprotic acid throughout this work.

Equilibrium constants refer to well-defined reactions, but do not necessarily provide evidence concerning the structures of the species involved in the reaction. Moreover, in the case of 2-thioorotic acid, tentative assignment of the calculated protonation constants to the functional groups present in the molecule is complicated by the difficulties in determining the predominant tautomeric forms existing in solution. The oxo and thio groups at the 2- and 4-positions can theoretically undergo keto-enol tautomerism and hence six tautomeric forms are possible (I to VI in Figure 1). Moreover, inter/intramolecular proton transfer from the carboxyl group to one of the heteroatoms can also occur giving several possible zwitterionic forms (*e.g.*, VII to IX in Figure 1). A large body of experimental evidence shows that uracil, thymine, and their nucleotides and nucleosides have a diketo structure in the solid state as well as in solution.[26] A spectroscopic study has shown that in the solid state 2-thioorotic acid adopts the keto-thione form[27] but it seems that several tautomeric forms may coexist in solution.[28]

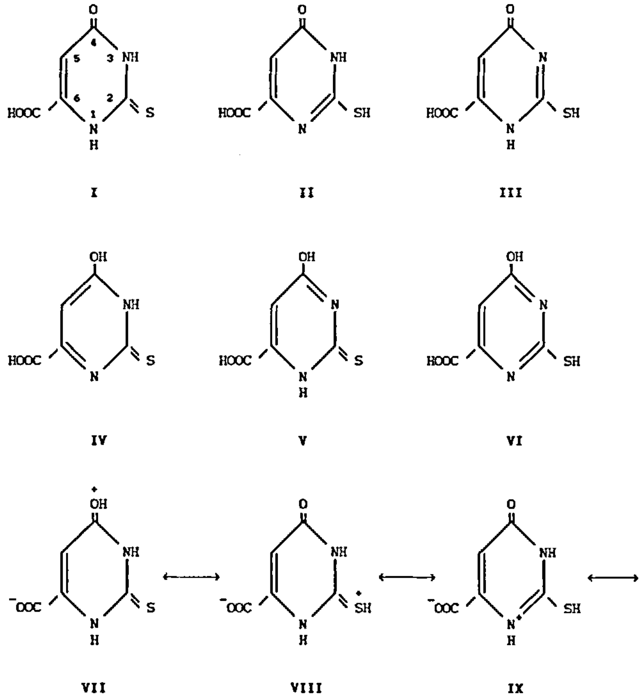


FIGURE 1 Possible tautomeric forms of 2-thioorotic acid.

The monoanion is presumably formed by the dissociation of a proton from the pyrimidine ring system (N1 or N3 proton). Uracil, 5-fluorouracil and thymine monoanions have been shown to exist in solution with a proton dissociated from either the N1 or N3 position.[25,29–30] The negative charge of these monoanions does not remain localized but is spread over the π-electron system of the pyrimidine ring. Similar behaviour may be expected for 2-thioorotic acid.

The second stepwise protonation constant corresponds to the dissociation of the proton of the carboxylate group. The negative charge may or may not remain localized in the functional group. In the case of TOA, the negative charge appears to be localized in the exocyclic carboxyl group because the protonation constant of the pyrimidine ring protons (N1 or N3) is similar to that of thiouracil (Table III).

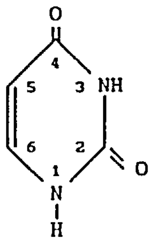
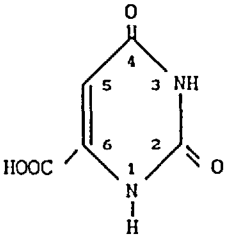
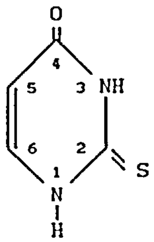
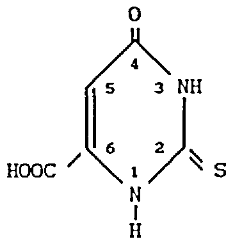
Comparison of the first stepwise protonation constants of TOA and 2-orotate shows differences similar to those found when comparing 2-thiouracil and uracil (Table III), thus indicating that the presence of a sulphur atom in position 2, as expected, increases the acidity of the molecule.

The Dimethylthallium(III)-TOA-H system

The system Me_2Tl^+–TOA–H^+ was studied by performing 6 titrations with initial metal concentrations in the range 0.5–8.0 mmol dm^{-3}. As mentioned earlier, the upper concentrations used were limited by the poor solubility of the ligand in water.

TABLE III

Literature protonation constants for the ligand and some related compounds. Formulae shown do not imply that any assertion is made about which is (are) the predominant tautomeric form(s) of the ligand present in solution.

Compound	pK values		Conditions[a]			Ref.
 URACIL	9.15	>13	s	?	?	31
	9.3		p	20°C	?	32
	9.51		p	25°C	0.1 M ?	33
	9.46(0.01)[b]		p	25°C	0	34
	9.74/9.14		p	10/40°C	0	35
	8.8(0.1)		p	45°C	0.1 M KNO_3	36
	9.7	14.2	s	25°C	3.0 M KCl	37
	9.16		p	30°C	0.1 M $NaClO_4$	38
	9.07/8.91/8.71		p	35/45/55°C	0.1 M KNO_3	39
	9.17		p	31°C	0.1 M KCl	40
	9.29(0.02)		p	25°C	0.1 M $NaNO_3$	41
 2-OROTIC ACID	2.8	9.45	s	?	?	31
	2.07	9.45	p	25°C	0.1 M KCl	42
	1.8(0.2)	9.55(0.15)	p	25°C	?	43
	2.30(0.03)	9.35(0.03)	p	20°C	0.15 M NaCl	44
	2.03(0.03)	9.38(0.02)	p	20°C	0.15 M NaCl	45
	2.09(0.1)	9.28(0.1)	p	25°C	0.5 M $NaClO_4$	46
	11.77(0.3)[c]	9.33(0.01)	p	25°C	0.1 M $NaNO_3$	47
 THIOURACIL	7.46/7.22/7.09		p	25/35/45°C	0.006 M ?	48
	7.71		p	35°C	0.1 M $NaClO_4$	49
 2-THIOOROTIC ACID	1.88	7.95	p	20°C	0.1 M KCl	50
	2.27(0.03)	7.90(0.03)	ps	20°C	0.15 M NaCl	44

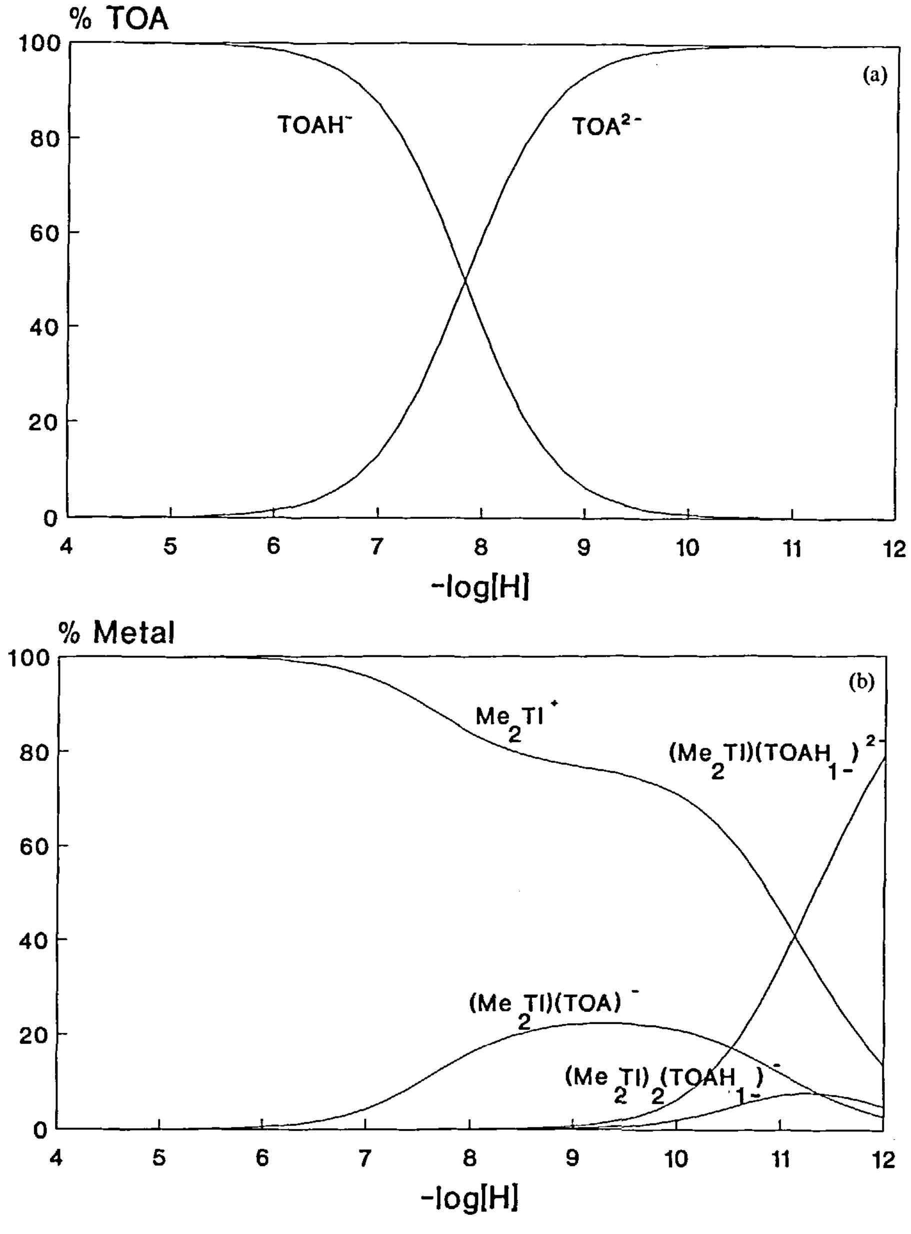
---

[a] Technique (p: potentiometry, s: spectrometry), temperature, ionic strength.

[b] Estimated error given by the authors in parentheses.

[c] Global protonation constant.

The individual metal formation curves did not overlap, suggesting that mononuclear complexes are not the only complexes formed in the system. The curves showed tails characteristic of the existence of hydroxo species. The maximum values of $\bar{p}$ obtained never exceeded 0.5 and the curves were ill-defined at the upper end. All these observations were confirmed by finding that the "best" model was the one formed by 110, 11–1, and 21–1 species. Twelve complexes and thirty models were tested to obtain the "best" model following our approach[25] including optimization and simulation in successive steps.



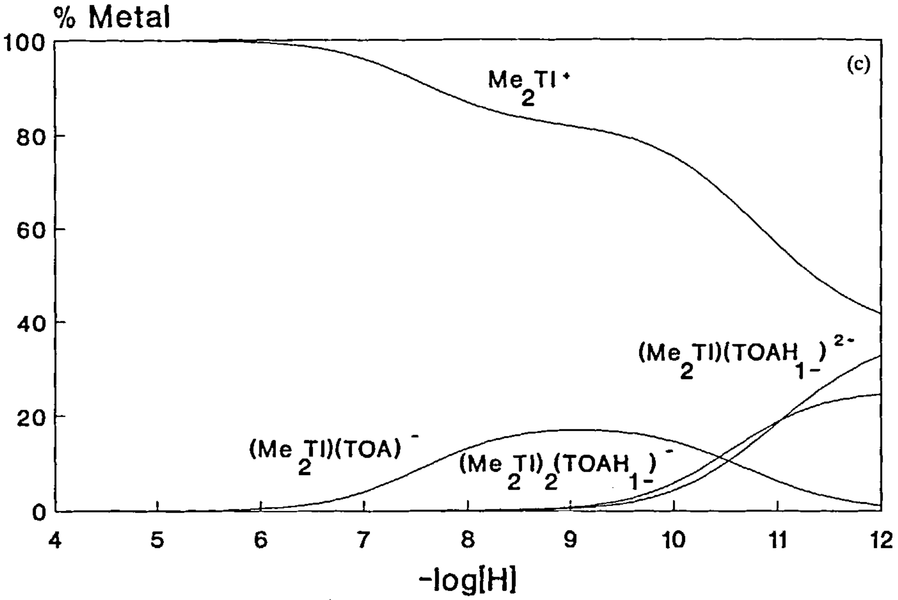


FIGURE 2 Species distributions as a function of $-\log[H]$; a: $C_{TOA} = 2.0$ mmol dm^{-3}; b: $C_{TOA} = 2.0$ mmol dm^{-3}, $C_{Me_2Tl^+} = 1.0$ mmol dm^{-3}; c: $C_{TOA} = 2.0$ mmol dm^{-3}, $C_{Me_2Tl^+} = 4.0$ mmol dm^{-3}.

The species distribution computed from the constants reported in Table II (Figure 2) shows that the 110 complex begins to form at $-\log[H] = 6$, *i.e.*, when the ligand starts losing its second proton, thus implying that for coordination to take place in solution the ionization of the carboxylate group is not enough. Although the 111 complex has been isolated in the solid form,[51] its negligible formation in water can be explained by the highly ionic character of the compound, which behaves as a 1 : 1 electrolyte in DMSO solution[51] (a medium whose dielectric constant is lower than water). The lack of coordination of dimethylthallium by the carboxylate group in the system under study is consistent with previous results.[12]

Very little information is available on metal–TOA complexes formed either in the solid phase[52–56] or in solution.[44] Various metal–ligand compounds, involving carboxylate, carbonyl, thiocarbonyl or nitrogen, have been described, principally based on ir spectroscopy. In fact, the loss of the second proton makes TOA behave like 2-thiouracil from a coordination viewpoint. Since Me_2Tl^+ has been shown to coordinate through a pyrimidinic nitrogen and the sulphur of the C=S group of the 2-thiouracil,[57] similar behaviour might be expected for the 110 complex formed with TOA. Participation of sulphur in coordination seems to be confirmed by the similarity in the value of the constant found (2.24) with that characteristic for the complexation of dimethylthallium(III) with a deprotonated thiol group (2.6).[12]

Above $-\log[H] = 9$, complexes 11–1 and 21–1 are formed; their relative concentrations depend on the ligand and metal concentrations present. The 11–1 complex is preferably formed when the ligand is in excess with respect to the metal. The nature of these species is difficult to establish. The formation of a binuclear complex is supported by the isolation of a compound with a stoichiometry of 2:1 at $-\log[H] =$

9.[51] This compound did not show the saline character of the monometallated compound. Formation of a 2:1 complex has also been described in the Ag(I)–TOA system.[52] From the potentiometric results it is not possible to deduce whether the 11–1 and 21–1 species are hydroxo species or compounds in which the ligand has undergone further deprotonation. *A priori*, both cases are possible; as already mentioned, the ligand has a third proton whose release may be favoured in the presence of a metal, but incorporation of a OH^- group to the coordination sphere of thallium should not be completely excluded, especially considering the relative high affinity of Me_2Tl^+ for OH^-.[18]

ACKNOWLEDGEMENTS

Financial support of this work by CAYCIT (PR84-0624) and DGICYT (PB87-0482) (Spain) is gratefully acknowledged.

REFERENCES

1. W.P. Ridley, L.J. Dizikes and J.M. Wood, *Science*, **197**, 329 (1978).
2. J.M. Wood, A. Chen, L.J. Dizikes, W.P. Ridley, S. Rakow and J.R. Lakowicz, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **37**, 16 (1978).
3. J.S. Thayer, *J. Organomet. Chem.*, **76**, 265 (1979).
4. F. Huber, U. Schmidt and H. Kirchmann, *ACS Symposium Series*, **82**, 65 (1978).
5. G. Agnes, S. Bendle, H.A.O. Hill, F.R. Williams and R.J.P. Williams, *Chem. Comm.*, 850 (1971).
6. G. Agnes, H.A.O. Hill, J.M. Pratt, S.C. Ridsdale, F.S. Kennedy and R.J.P. Williams, *Biochim. Biophys. Acta*, **252**, 207 (1971).
7. F. Huber and H. Kirchmann, *Inorg. Chim. Acta*, **29**, L249 (1978).
8. P.J. Craig, in "The Handbook of Environmental Chemistry", Vol. 1 Part A, Ed. O. Hutzinger, (Springer, Berlin, 1980), p. 169.
9. A.G. Lee, "The Chemistry of Thallium", (Elsevier, Amsterdam, 1971).
10. C.R. Hart and C.K. Ingold, *J. Chem. Soc.*, 4372 (1964).
11. J.R. Cook and D.F. Martin, *J. Inorg. Nucl. Chem.*, **26**, 1249 (1964).
12. M. García Bugarín, M.E. García, G. Berthon, J.S. Casas and J. Sordo, *Polyhedron*, **7**, 2487 (1988).
13. M.S. García-Tasende, M. García Bugarín and M. Filella, *Polyhedron*, **10**, 517 (1991).
14. H. Gilman and R.G. Jones, *J. Am. Chem. Soc.*, **68**, 517 (1946).
15. G.D. Shier and R.S. Drago, *J. Organomet. Chem.*, **5**, 330 (1966).
16. D. Dyrssen, D. Jagner and F. Wengelin, "Computer Calculation of Ionic Equilibria and Titration Procedures with specific Reference to Analytical Chemistry", (Almqvist and Wiksell, Stockholm, 1968).
17. P.W. Linder, R.G. Torrington and D.R. Williams, "Analysis using Glass Electrodes", (Open University Press, Milton Keynes, 1984).
18. J.K. Laurence and J.E. Prue, *J. Sol. Chem.*, **3**, 553 (1974).
19. P.M. May, K. Murray and D.R. Williams, *Talanta*, **32**, 483 (1985).
20. P.M. May, K. Murray and D.R. Williams, *Talanta*, **35**, 825 (1988).
21. P.M. May and K. Murray, *Talanta*, **35**, 927 (1988).
22. P.M. May and K. Murray, *Talanta*, **35**, 933 (1988).
23. M. Filella and D.R. Williams, *Inorg. Chim. Acta*, **106**, 49 (1985).
24. E. Casassas, M. Filella and R. Tauler, *Anal. Chim. Acta*, **191**, 413 (1986).
25. M. Filella, N. Garriga and A. Izquierdo, *Talanta*, **34**, 971 (1987).
26. J.S. Kwiatkowski and B. Pullman, *Adv. Heterocycl. Chem.*, **18**, 199 (1975).
27. G.S. Pandey, P.C. Nigam and U. Agarwala, *J. Inorg. Nucl. Chem.*, **39**, 1877 (1977).
28. M.V. Jovanovic and E.R. Biehl, *J. Heterocycl. Chem.*, **24**, 191 (1987).
29. I. Wempen and J.J. Fox, *J. Am. Chem. Soc.*, **86**, 2474 (1964).
30. K.L. Wierzchowski, E. Litonska and D. Shugar, *J. Am. Chem. Soc.*, **87**, 4621 (1965).
31. D. Shugar and J.J. Fox, *Biochim. Biophys. Acta*, **9**, 199 (1952).
32. P. Bamberg and P. Hemmerich, *Helv. Chim. Acta*, **44**, 1001 (1961).

33. K. Nakanishi, N. Suzuki and F. Yamazaki, *Bull. Chem. Soc. Japan*, **34**, 53 (1961).
34. J.J. Christensen, J.H. Rytting and R.M. Izatt, *J. Phys. Chem.*, **71**, 2700 (1967).
35. J.J. Christensen, J.H. Rytting and R.M. Izatt, *J. Chem. Soc. (B)*, 1643 (1970).
36. M.M. Taqui Khan and C.R. Krishnamoorthy, *J. Inorg. Nucl. Chem.*, **36**, 711 (1974).
37. J.R. DeMember and F.A. Wallace, *J. Am. Chem. Soc.*, **97**, 6240 (1975).
38. R.C. Srivastava and M.N. Srivastava, *J. Inorg. Nucl. Chem.*, **40**, 1439 (1978).
39. K. Ramalingam and C.R. Krishnamoorthy, *Inorg. Chim. Acta*, **67**, 167 (1982).
40. B.S. Sekhon, *J. Indian Chem. Soc.*, **64**, 308 (1987).
41. R. M'Boungou, M. Pettit-Ramel, G. Thomas-David, G. Perichet and B. Pouyet, *Can. J. Chem.*, **67**, 973 (1989).
42. E.R. Tucci, E. Doody and N.C. Li, *J. Phys. Chem.*, **65**, 1570 (1961).
43. E.M. Woolley, R.W. Wilton and L.G. Hepler, *Can. J. Chem.*, **48**, 3249 (1970).
44. N.K. Davidenko and N.N. Zinich, *Koord. Khim.*, **5**, 1 (1979).
45. N.N. Vlasova and N.K. Davidenko, *Russ. J. Inorg. Chem.*, **27**, 1599 (2823) (1982).
46. J. Maslowska and A. Dorabialski, *Polish J. Chem.*, **57**, 1089 (1983).
47. R. M'Boungou, M. Pettit-Ramel, G. Thomas-David, G. Perichet and B. Pouyet, *Can. J. Chem.*, **65**, 1479 (1987).
48. E.R. Garrett and D.J. Weber, *J. Pharm. Sci.*, **59**, 1383 (1970).
49. K. Srivastava and M.N. Srivastava, *Nat. Acad. Sci. Letters*, **5**, 197 (1982).
50. F. Capitán, M. Román and A. Arrebola, *Inform. Quim. Anal.*, **25**, 111 (1971).
51. M.S. García-Tasende, B.E. Rivero, A. Castiñeiras, A. Sánchez, J.S. Casas, J. Sordo, W. Hiller and J. Strähle, *Inorg. Chim. Acta*, **181**, 43 (1991).
52. F. Capitán, M. Román and A. Arrebola, *Inform. Quim. Anal.*, **26**, 135 (1972).
53. G.S. Pandey, G.C. Pandey, P.C. Nigam and U. Agarwala, *Indian J. Chem.*, **14A**, 884 (1976).
54. G.S. Pandey, G.C. Pandey, P.C. Nigam and U. Agarwala, *Indian J. Chem.*, **15A**, 537 (1977).
55. G.S. Pandey, P.C. Nigam and U. Agarwala, *Indian J. Chem.*, **17A**, 74 (1979).
56. M. Srivastava and G.S. Pandey, *Indian J. Chem.*, **27A**, 477 (1988).
57. M.S. García-Tasende, M.I. Suárez, A. Sánchez, J.S. Casas, J. Sordo, E.E. Castellano and Y.P. Mascarenhas, *Inorg. Chem.*, **26**, 3818 (1987).