Nitrosonium Tetranitratothallate(III)

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Summary The compound $NO^+Tl(NO_3)_4^-$ has been prepared; its structural assignment is based on elemental analysis, i.r. spectra, and electrical conductivity measurements.

COMPOUNDS containing ions of general formula $M(NO_3)_4^-$ are well characterised for several elements in the 3+ oxidation state.[1,2] I report the preparation and initial investigation of a new compound of this type, nitrosonium tetranitratothallate(III), $NO^+Tl(NO_3)_4^-$.

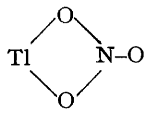
The compound was prepared by condensing dinitrogen pentoxide (20 g.) on to $TlNO_3$ (3 g.) at −78°; the solid reactants were intimately mixed and allowed to warm to room temperature. After 3 days, the excess of nitrogen oxides was removed by pumping (10^{-3} mm.), leaving the compound $NO^+Tl(NO_3)_4^-$ as a white free flowing powder. The compound is extremely hygroscopic, necessitating stringent precautions to exclude moisture during both preparation and subsequent handling.

Thallium was determined gravimetrically as Tl_2CrO_4 after reduction of the Tl^{III} compound to Tl^I with SO_2. Nitrogen was determined by the reductive Kjeldahl method. Analyses were satisfactory for $NO^+Tl(NO_3)_4^-$.

Hydrolysis of the compound with 2M-NaOH solution yields a black precipitate, believed to be hydrated Tl_2O_3, together with a solution containing nitrate ions only. It was established from the u.v. spectrum of this solution that five NO_3^- ions were liberated for each molecule of $NO^+Tl(NO_3)_4^-$ hydrolysed (ϵ_{303} 34·5). Nitrite ion is likely to be formed initially from NO^+ hydrolysis; however, this will be rapidly oxidised to NO_3^- in the presence of freshly precipitated Tl_2O_3. This contrasts with the alkaline hydrolysis of $NO^+Fe(NO_3)_4^-$ in which NO_2^- and NO_3^- are found in the ratio 1 : 4,[3] the difference arising from the inability of Fe_2O_3 to oxidise NO_2^- to NO_3^-.

The formulation of $NO^+Tl(NO_3)_4^-$ as an ionic salt, rather than as an adduct of $Tl(NO_3)_3$ with N_2O_4,[3] receives direct support from electrical conductivity measurements. In acetonitrile solution, $NO^+Tl(NO_3)_4^-$ behaves as a typical weak electrolyte; the molar conductivity of a 10^{-3}N-solution ($\Lambda = 76{\cdot}5$ ohm^{-1}cm^2) is of similar magnitude to that observed for other 1 : 1 electrolytes in acetonitrile solution.[3]

I.r. spectra were recorded of both Nujol and fluorocarbon mulls of the compound. The observed bands are empirically assigned in terms of a model containing bidentate nitrate groups.[3,4]



2300	m	sp	NO^+
1670	s	br	N–O str.
1282 1265	s	br	NO_2 antisymmetric str.
1025 958	m	br	NO_2 symmetric str.
778 750 720 688	m	sp	NO_3 deformations + Tl–O str.

Repeated scanning of the Nujol mull spectrum was accompanied by the appearance of new bands in the spectrum, consistent with oxidation and nitration of the mulling agent.[5]

Two important considerations arise from the i.r. spectra and reactivity of $NO^+Tl(NO_3)_4^-$. Firstly, the stretching frequency assigned to the terminal N=O groups (1670 cm^{-1}) is the highest value reported for a nitrate group co-ordinated in bidentate fashion. This is at first surprising, since on the basis of charge-radius ratios, Tl^{III} would be expected to be less strongly polarising than either Ti^{IV} or Sn^{IV}, in which the corresponding frequencies are 1635 and 1622 cm^{-1}, respectively.[4] This observation can be explained adequately by consideration of the underlying electron shells of the metals; Tl^{III} $4f^{14}5d^{10}$, Sn^{IV} $4d^{10}$, Ti^{IV} $3s^23p^6$. For Tl^{III}, the effective nuclear charge experienced by the nitrato-group will be greater than that of the Group IV metals due to the interpolation of the poorly shielding $4f^{14}$ shell. This interpretation is probably an over-simplification; however, it does serve as a good illustration of normal-co-ordinate analysis calculations[6] in which it was shown that effects of polarisation of the nitrate group by the metal are at least an order of magnitude more important than either the metal–oxygen force constant or the mass of the metal, in determining the stretching frequencies of the bidentate nitrate group.

In the absence of either single-crystal *X*-ray data, or detailed Raman spectra, suggestions as to the structure of $Tl(NO_3)_4^-$ can only be speculative. However the frequency and number of observed bands in the i.r. spectrum is reminiscent of the spectra observed for $Ti(NO_3)_4$ and $Sn(NO_3)_4$; therefore a similar structure consisting of four bidentate nitrate groups symmetrically bonded to the metal in pseudotetrahedral fashion (point group D_{2d}) is suggested. A planar arrangement of oxygen atoms about the Tl atom, as is found[2] in $Au(NO_3)_4^-$, is unlikely; the gold compound undoubtedly derives its planar co-ordination from the underlying d^8 shell. If attempts to prepare single crystals of salts containing $Tl(NO_3)_4^-$ ion are successful, *X*-ray data will be reported in a future publication.

The chemical reactivity of $NO^+Tl(NO_3)_4^-$ towards many organic compounds (diethyl ether, aniline, benzene, *etc.*) resembles that of other nitrato-compounds which have been shown to contain bidentate nitrate groups. The ready availability of the 1+ oxidation state for thallium, combined with bidentate co-ordination, satisfies the requirement of the mechanism suggested by Addison[7] in which release of the highly reactive NO_3 radical is accompanied by reduction of the metal. For $Tl(NO_3)_4^-$ the initial step would be

$$Tl^{III}(NO_3)_4^- \rightarrow Tl^{I}(NO_3)_2^- + 2NO_3.$$

Attempted preparation of isoelectronic $Pb(NO_3)_4$ by condensation of N_2O_5 on to $Pb(NO_3)_2$ was unsuccessful; $Hg(NO_3)_4^{2-}$, which is also isoelectronic with $Tl(NO_3)_4^-$, is accessible by a different synthetic route.[8]

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