

Nitronium Tetranitratogallate(III)

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Summary The new volatile complex $\text{NO}_2^+\text{Ga}(\text{NO}_3)_4^-$ has been prepared by the novel synthetic route;
 $\text{NO}^+\text{GaCl}_4^- + 5\text{N}_2\text{O}_5 \rightarrow \text{NO}_2^+\text{Ga}(\text{NO}_3)_4^- + 4\text{NO}_2\text{Cl} + \text{N}_2\text{O}_4$.

DINITROGEN PENTOXIDE adducts of a number of anhydrous metal nitrates are now known and vibrational spectroscopy indicates that formulation as nitronium salts of nitrate-anions is appropriate for all such species studied to date.¹ The volatility of dinitrogen pentoxide adducts does not, however, appear to be a general phenomenon, although the adduct $\text{Hf}(\text{NO}_3)_4 \cdot \text{N}_2\text{O}_5$ is reported to be volatile² and a sublimate is obtained on heating $\text{Al}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_5$ [$\text{NO}_2^+\text{Al}(\text{NO}_3)_4^-$] to 70 °C in vacuum (10^{-2} mm).^{3,4} Maintenance of

the 1:1 $\text{Al}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_5$ stoichiometry is, however, dependent on the experimental conditions.³ We have now isolated the new compound $\text{NO}_2^+\text{Ga}(\text{NO}_3)_4^-$ which yields a sublimate of identical composition at 70 °C and 10^{-2} mm. This compound is the first anhydrous nitrate-complex of gallium to be reported.

The compound was prepared by direct reaction of $\text{NO}^+\text{GaCl}_4^-$ and N_2O_5 . $\text{NO}^+\text{GaCl}_4^-$ was prepared by condensing dry NOCl on to anhydrous GaCl_3 .⁵ The resulting red solution was maintained at -10 °C for some hours, followed by removal of the excess of NOCl , to leave a white free-flowing powder.

Pure, dry N_2O_5 was condensed on to $\text{NO}^+\text{GaCl}_4^-$ at -78 °C; the solid reactants were mixed by shaking and

allowed to warm to room temperature. Reaction commenced immediately and was complete in *ca.* one day. The excess of N_2O_5 and gaseous products was removed by evacuation (10^{-2} mm) at room temperature. The resulting white powder was identified as $NO_2^+Ga(NO_3)_4^-$ by total nitrogen and gallium analysis. Nitrogen was determined by the reductive Kjeldahl method and gallium by edta titration. As expected, the compound is very hygroscopic and atmospheric moisture was excluded during its preparation and in all subsequent investigations.

The compound is insoluble in non-polar solvents such as carbon tetrachloride but soluble to differing extents in most polar solvents some of which undergo vigorous reaction, in particular the lower alcohols.

Reactions of the nitrosonium tetrachlorometallates $NO^+AlCl_4^-$ and $NO^+FeCl_4^-$ with N_2O_5 , recently carried out in these laboratories, have also been found to yield the corresponding nitronium tetranitratometallates and this appears to be a synthetic route of general applicability.

Sublimation of $NO_2^+Ga(NO_3)_4^-$ at $70^\circ C$, 10^{-2} mm yielded a product of similar analysis to the starting material possessing an identical i.r. spectrum and X-ray powder photograph. No evidence for the formation of the anhydrous salt, $Ga(NO_3)_3$, was obtained under these conditions.

The i.r. spectrum of the sublimed product (Nujol mull) contained the following principal bands (cm^{-1}): 2377s sp, 2357m sp [$\nu_3(NO_2^+)$]; 1687s b; 1621s b, 1572s b [$\nu_4(NO_3)$]; 1305vs b [$\nu_1(NO_3)$]; 972s b [$\nu_2(NO_3)$]; 784s b, 778s sh [$\nu_6(NO_3)$]; 742s [$\nu_3(NO_3)$]; 716m sp [$\nu_5(NO_3)$]; 576m sp [$\nu_2(NO_2^+)$].

Rapid attack of Nujol by $NO_2^+Ga(NO_3)_4^-$ was evident. The quoted assignments, appropriate to unidentate nitrate co-ordination,⁶ are supported by complementary Raman evidence. The Raman spectrum (He-Ne laser) of a powdered sample consisted of the following bands (cm^{-1}): 1581m b [$\nu_4(NO_3)$]; 1401m sp [$\nu_1(NO_2^+)$]; 1305s sp [$\nu_1(NO_3)$]; 994vs sp [$\nu_2(NO_3)$]; 779w b [$\nu_6(NO_3)$]; 719w sp [$\nu_5(NO_3)$].

No evidence for the presence of ionic nitrate was obtained and representation of the compound as $NO_2^+Ga(NO_3)_4^-$ is thus in accord with the vibrational spectra. Furthermore, the relative intensities of the three highest energy nitrate fundamentals in the Raman spectrum is the feature⁷ indicative of unidentate nitrate co-ordination of gallium. This is in contrast to the symmetrically bidentate nitrate bonding in, and overall dodecahedral (D_{2d}) geometry of, the $Fe(NO_3)_4^-$ anion, established by an X-ray study of the Ph_4As^+ salt.⁸ Both $Ga^{3+}(3d^{10})$ and $Fe^{3+}(3d^5)$ have spherically symmetrical electronic configurations which usually favour symmetrically bidentate bonding of nitrate groups.⁷ However, the octahedral ionic radius of Ga^{3+} (0.62 Å) is slightly smaller than that of Fe^{3+} (0.64 Å) and no eight-co-ordinate gallium(III) species have yet been observed. On the other hand, tetrahedral co-ordination is well known for gallium(III). Further investigations of the vibrational spectra of $NO_2^+Ga(NO_3)_4^-$ and attempts to produce single crystals for X-ray studies are in progress.

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