Tetranitratoaurates(III): Preparation, Spectra, and Properties

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Reactions of gold and some of its compounds with nitrogen(IV) and nitrogen(V) oxide systems have given rise to the series of compounds $MAu(NO_3)_4$ (M = Na, K, Rb, Cs, NO_2, and NO). In the potassium salt all four nitrate groups in the anion are known to be bonded in the same unidentate manner, providing the first authenticated example of a square-planar complex containing only unidentate nitrate ligands. The vibrational spectra and properties of the tetranitratoaurates(III) are discussed in the light of this structure.

THE known nitrate chemistry of gold at the commencement of this work was limited and generally ill-characterised. Hanriot and Raoult[1] claimed to have prepared a hydrated gold(III) nitrate of composition $Au(NO_3)_3,nH_2O$ but so far, it has not been possible to repeat this work. A study of the products obtained from solutions of 'gold(III) hydroxide' in nitric acid by Schottlander[2] resulted in the identification of the trihydrated complex acid $HNO_3,Au(NO_3)_3,3H_2O$, alternatively formulated as $HAu(NO_3)_4,3H_2O$. Also, the anhydrous products $MAu(NO_3)_4$ (M = K, Rb, Tl, or NH_4) were obtained as well as further compounds of composition $HM_2Au(NO_3)_6$ (M = K, Rb, or NH_4). The characterisation of these compounds as nitrato-complexes rather than double salts however, was not possible at that time. The preparation of the salt $[Au(NH_3)_4](NO_3)_3$ was claimed by Weitz[3] but attempts to reproduce this work during the course of the present studies have failed. More recently, Field and Hardy[4] claim to have prepared, in extremely small yield, volatile, moisture-sensitive, anhydrous gold(III) nitrate. The identity of this compound was inferred from its gold content alone and no further properties were discussed.

No simple nitrate of univalent gold is known although ionic compounds of the type $Au(tu)_2NO_3,H_2O$[5] (tu = thiocarbamide) and $Au(etu)_2NO_3$[6] (etu = ethylenethiocarbamide) have been prepared. The nitrato-complex $Au(NO_3),PPh_3$ has recently been obtained and characterised.[7]

EXPERIMENTAL

Preparation of Compounds

Potassium Tetranitratoaurate(III).—A large excess of pure dinitrogen pentoxide (10—15 g) was condensed onto finely ground crystals of anhydrous potassium tetrabromoaurate(III) (1 g) at −78°. On warming to room temperature with shaking, bromine vapour was evolved as reaction took place. After 12 h, excesses of nitrogen oxides were removed *in vacuo* and the product was a pale yellow powder. The compound was recrystallised in anhydrous form from pure nitric acid solution without decomposition [Found: K, 8·8; Au, 40·1; N, 11·8. $KAu(NO_3)_4$ requires K, 8·1; Au, 40·7; N, 11·6%].

Nitronium Tetranitratoaurate(III).—(a) *From gold metal.* An excess of 'liquid' dinitrogen pentoxide was distilled onto freshly precipitated gold powder (1 g) at −78°. The mixture was allowed to warm to room temperature and was then refluxed for four days (using methanol at −15° as coolant). Unchanged particles of gold were then removed by filtration under nitrogen, and the filtrate was left to evaporate to dryness in the absence of atmospheric moisture. Large golden-yellow crystals were produced [Found: Au, 39·9; N, 14·3; gold : nitrate ratio calculated from an alkaline hydrolysate of the compound, 1 : 5·0. $NO_2Au(NO_3)_4$ requires Au, 40·1; N, 14·3%; gold : nitrate ratio 1 : 5·0]. The product slowly decomposed even under dry nitrogen, forming a surface coating of gold metal with the evolution of nitrogen oxides. Decomposition was rapid in moist air with the copious evolution of white fumes.

In an alternative procedure, a gaseous dinitrogen pentoxide–ozone mixture was passed through an agitated fuming nitric acid solution (100 ml) containing gold powder (1 g) for 6 h at room temperature. Filtration, with subsequent slow evaporation yielded large yellow crystals of the nitronium salt.

(b) *From gold*(III) *chloride.* An excess of 'liquid' dinitrogen pentoxide (20 g) was condensed onto anhydrous gold(III) chloride (1 g) at −78°. On warming to room temperature with constant stirring, a clear solution consisting of two distinct phases was obtained. After a few hours, a finely divided yellow precipitate formed and was removed by filtration under dry nitrogen. The pale yellow powder was analysed and found to be of composition $Au(NO_3)_3,0{\cdot}6N_2O_5$. The clear yellow filtrate gave rise to large crystals of nitronium tetranitratoaurate(III). It appears likely that the yellow precipitate formed in this reaction was a finely divided form of the nitronium salt, thrown out of solution owing to solubility factors. In such form, loss of nitrogen oxides might reasonably occur more rapidly than in the case of large crystals, and thus give rise to the apparently non-stoicheiometric composition.

When samples of gold(I) chloride, gold(III) chloride, and tetrachloroauric(III) acid were reacted individually with pure dinitrogen pentoxide, the product isolated after rapid removal of excess volatiles by evacuation was invariably a finely divided, yellow powder of the variable composition, $Au(NO_3)_3,xN_2O_5$ ($x = 0{\cdot}5$—$1{\cdot}0$). Again, the apparent non-stoicheiometry of these products could be attributed to the readiness of the nitronium salt to evolve oxides of nitrogen when in a sub-divided state.

$NOAu(NO_3)_4$.—The nitrosonium salt was obtained by treatment of nitronium tetranitratoaurate(III) with dinitrogen tetroxide in dry nitromethane. The nitronium

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[1] A. Hanriot and R. M. Raoult, *Compt. rend.*, 1912, **155**, 1086.

[2] P. Schottlander, *Annalen*, 1883, 217; Diss. Wurtzburg, 1884.

[3] E. Weitz, *Annalen*, 1915, **410**, 117.

[4] B. O. Field and C. J. Hardy, *J. Chem. Soc.*, 1964, 442.

[5] G. T. Morgan and W. Ledbury, *J. Chem. Soc.*, 1922, 2833.

[6] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1928, 143.

[7] L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Co-ordination Chem. Rev.*, 1966, **1**, 255.

salt has a high solubility in nitromethane but slowly decomposes, even in dilute solution, to form a metallic gold mirror. This decomposition does not, however, preclude the use of nitromethane as a preparative medium.

A small amount of nitronium tetranitratoaurate(III) (0·1 g) was dissolved in dry nitromethane (2 ml). An excess of dry dinitrogen tetroxide (25 ml) was added, and on cooling, crystals of the nitrosonium salt were precipitated. These were rapidly removed from the solution by filtration and washed with dinitrogen tetroxide before drying in a static vacuum and transference to the dry box [Found: Au, 41·2; N, 14·3; ratio of gold : nitrate : nitrite from alkaline hydrolysate, 1 : 4·1 : 0·9. $NOAu(NO_3)_4$ requires Au, 41·5; N, 14·7%; ratio of gold : nitrate : nitrite, 1 : 4 : 1]. The nitrosonium salt was stable in a dry atmosphere but rapidly evolved brown fumes in the presence of moisture.

$MAu(NO_3)_4$. (M = Na, K, Rb, Cs).—The nitronium salt was found to be an extremely useful and convenient starting material for the preparation of a variety of tetranitratoaurate(III) salts. The reactions by which these salts may be prepared are summarised by the equation:

$$NO_2Au(NO_3)_4 + MNO_3 \xrightarrow{HNO_3} MAu(NO_3)_4 + N_2O_5$$

M, in this case, is a univalent cation. The method of preparation described here for the caesium salt is identical with that used for the other cations.

Large crystals of nitronium tetranitratoaurate(III) (0·2 g, 0·41 mmol) were dissolved in fuming nitric acid. To this solution, a stoicheiometric quantity of caesium nitrate (0·08 g, 0·41 mmol) was added. On cooling, crystals of the compound $CsAu(NO_3)_4$ were formed. These were removed by filtration under nitrogen and dried in static vacuum.

Materials and Reagents.—Gold metal of high purity was obtained from Johnson, Matthey and Co. Ltd. Finely divided gold powder was prepared from acidic solutions of gold(III), using hydroquinone as the reducing agent.[8] Gold(III) chloride was produced from the direct chlorination of gold, and gold(I) chloride was obtained by thermal decomposition of the trichloride. Potassium tetrabromoaurate(III) [8] and tetrachloroauric(III) acid tetrahydrate [9] were prepared from gold metal by standard methods. Dinitrogen tetroxide was prepared by the method of Addison [10] and required no further purification. Dinitrogen pentoxide was prepared by the dehydration of fuming nitric acid by phosphoric oxide in a stream of ozonised oxygen. The preparation of 'liquid' dinitrogen pentoxide was effected by the dehydration of fuming nitric acid by phosphoric oxide in a stream of dry nitrogen. Collection was at −78°, and the product was a mixture of dinitrogen pentoxide, tetroxide, and nitric acid in variable proportions. Organic solvents were dried by accepted methods.[11] Reactions were carried out in vessels protected by phosphoric oxide guard tubes, and all products were handled exclusively in a dry box.

Analyses.—The gold content of those compounds which contained no alkali-metal cation was obtained by direct ignition to the metal in silica micro-crucibles. In the case of the alkali-metal salts, the compounds were first decomposed using distilled water, and the precipitates so obtained were removed and collected by filtration and ignited to metallic gold. Total nitrogen content was determined by a modified Kjeldahl method using Devarda's alloy. Alkaline hydrolysates were prepared by the 'closed-bottle' technique in the presence of a known volume of 2M-sodium hydroxide. Quantitative u.v.-visible measurements for the nitrate ion concentration in the alkaline hydrolysates were made on a Unicam SP 500 spectrophotometer. Nitrite was estimated by the back-titration of ceric sulphate solution with standard ferrous ammonium sulphate. Alkali metals were determined by flame photometry.

Magnetic Susceptibility.—Measurements were made on finely divided samples at room temperature by the Gouy method.

Conductivity Measurements.—These were carried out at 0° in a Pyrex cell containing electrodes of bright platinum.

X-*Ray Powder Photographs.*—Data were obtained using a Phillips X-ray powder diffractometer with an 11-cm camera and Cu-K_α radiation.

Vibrational Spectroscopic Measurements.—Infrared spectra were recorded on P.E. 521 and 457 spectrophotometers. Nujol mulls were prepared in a dry box and mounted between silver chloride windows. Raman spectra were obtained using the Cary 81 spectrophotometer, with a helium-neon gas laser attachment.

RESULTS AND DISCUSSION

Nitronium and nitrosonium tetranitratoaurates(III) are extremely sensitive to moisture, decomposing to produce oxides of nitrogen and residual gold metal. They also display marked reactivity to a variety of dry organic solvents; the nitronium salt, in particular, has been observed to react explosively with dimethyl sulphoxide and acetonitrile. Such reactivity is undoubtedly due to the high chemical reactivity of the nitronium ion. Both the nitronium and nitrosonium salts readily dissolve in nitromethane but with slow decomposition and concomitant formation of gold mirrors. In dilute solutions, decomposition was slow enough to permit useful conductivity measurements. All the tetranitratoaurates(III) readily dissolve in concentrated nitric acid and with the exception of the nitronium salt recrystallise unchanged from such solutions. The nitronium salt however recrystallises only from nitric acid of concentration greater than 95%; more dilute nitric acid yields crystals of the complex hydrated acid $HAu(NO_3)_4,3H_2O$. Prolonged evacuation of the nitronium salt at room temperature resulted in conversion into a compound empirically $Au_2O(NO_3)_4$ [Found: Au, 59·1; N, 8·0. $Au_2O(NO_3)_4$ requires: Au, 59·9; N, 8·5%].

The range of alkali-metal salts prepared showed a pronounced gradation in chemical stability and resistance to attack by moisture. The caesium salt was by far the most stable compound and could be handled in the atmosphere without appreciable decomposition.

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[8] B. P. Block, *Inorg. Synth.*, 1953, **4**, 14.

[9] G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' Academic Press, New York, 1965, vol. II, p. 1056.

[10] C. C. Addison and R. Thompson, *J. Chem. Soc.*, 1949, S. 218.

[11] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jun., 'Technique of Organic Chemistry,' Interscience, 1955, vol. VII.

In contrast, the sodium salt was prone to decomposition even within the dry box. This effect is presumably related to the influence of cationic size upon the stability of the crystal lattice. After prolonged atmospheric exposure, the decomposition products were found to be the alkali-metal nitrate and gold metal. In most of the organic solvents used in these studies, the alkali-metal salts remained both passive and insoluble.

A single crystal *X*-ray study has shown that the potassium salt consists of discrete potassium and tetranitratoaurate(III) ions.[12] The gold ion is co-ordinated in a square-planar manner to four equivalent nitrate groups in unidentate fashion, with the four gold–oxygen bond distances of average length 2·0 Å. The nitrate groups are of C_s local symmetry, and combine in the anion to give overall C_{2h} symmetry.

Magnetic susceptibility measurements carried out in these laboratories at room temperature on the finely divided potassium salt showed the compound to be diamagnetic. This is in accordance with the crystal structure, and is compatible with the preferred square planar four-co-ordination of the d^8 gold(III) ion.

Infrared and Raman Spectra.—A review of recent crystallographic studies suggests that, wherever possible, the nitrate group tends to co-ordinate in a symmetrical, bidentate manner to metal cations.[13] There are few established examples of complexes containing the unidentate nitrate group but in those cases where structural information is available, it is invariably found that the M–O–N unit is bent, with a bond angle of *ca.* 114°.[13] In each of the observed bonding situations of the nitrate group (unidentate, bidentate, or bridging) co-ordination serves to lower the symmetry of the D_{3h} ion in such a way that the degeneracy of the ionic E' vibrational modes is lifted. Normal co-ordinate calculations for the bidentate nitrate unit MO_2NO [14] and also for the related carbonato-unit MO_2CO [15] have indicated that in such small ' chelate rings ' the concept of group frequencies is no longer applicable. Such results predict extensive mixing of the nitrate vibrations, particularly between the symmetrical modes of MO_2 stretching and NO_3 deformation. Similar calculations on the unidentate molecular units $MONO_2$ [16] and $MOCO_2$,[15] both of C_s symmetry indicate less mixing between the internal vibrations and consequently a simpler spectral assignment is justified.

The infrared and Raman spectra obtained for the tetranitratoaurates(III) are listed in Tables 1 and 2 respectively. (Satisfactory Raman spectra could not be obtained for the sodium and rubidium salts which decomposed in the laser beam.) The spectra are assigned considering the vibrations of a single $AuONO_2$ unit under C_s symmetry, the regions of absorption being those expected for a unidentate nitrate group co-ordinated to a highly polarising cation.[17]

The band splittings observed only in the vibrational spectra of the solid tetranitratoaurates(III) are probably attributable to crystal-lattice effects in which case the fine structure could be accounted for by factor-group analysis. This is possible for the potassium salt of known crystal structure [12] but has not been attempted here. An alternative interpretation of the band splittings in the solids in terms of intramolecular interactions within the $Au(NO_3)_4^-$ unit of overall C_{2h} symmetry is possible but less plausible in view of the splitting also observed for NO_2^+.

It can be seen (Table 1) that the caesium salt displays an i.r. spectrum of considerable complexity. A similar effect has been observed in the i.r. spectra of the compounds, $M_2Co(NO_3)_4$ (M = Na, K, Rb, Cs).[18] In the latter case, however, the spectrum of the sodium salt contained additional bands which were ascribed to a structural change in the series of compounds resulting from factors related to cationic size.

The spectra of nitronium and nitrosonium tetranitratoaurate(III) display bands characteristic of the NO_2^+ and NO^+ ions respectively. The nitronium salt, instead of giving rise to single absorptions at *ca.* 2360 and 570 cm^{-1}, characteristic of the antisymmetric stretching and degenerate bending modes of NO_2^+ exhibits well-defined doublets in these regions. Again an explanation can be sought from a factor-group study when a full *X*-ray analysis of the nitronium salt becomes available.

In the nitrosonium salt, the NO^+ absorption appears as a sharp peak of medium intensity at 2288 cm^{-1} in the i.r. region, and in the Raman as a weak, broad band at 2300 cm^{-1}. Its vibrational frequency is thus little removed from that expected of the free ion.[19] The i.r. spectra of the NO_2^+ and the NO^+ compounds, and the Raman spectrum of the NO_2^+ compound were also recorded for fresh solutions in nitromethane (Tables 1 and 2). The i.r. spectra provide strong evidence for the presence of the NO_2^+ and NO^+ ions in solution, and these spectra together with the Raman spectrum indicate the presence of the $Au(NO_3)_4^-$ anion in nitromethane. These solutions slowly decompose, but evidence for the presence of the NO_2^+ and NO^+ ions persists for 30 h. As the i.r. bands assignable to these ions diminish with time, new bands characteristic of a solution of dinitrogen tetroxide develop in the spectrum (Table 1). The Raman spectrum of a solution of $KAu(NO_3)_4$ in 100% nitric acid (Table 2) indicates the persistance of $Au(NO_3)_4^-$ in this medium also, though the polarisation data obtained from the Raman solution studies were seriously restricted in value by interfering solvent bands.

The intense bands at 360 (Raman) and 378 cm^{-1} (i.r.)

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[12] C. D. Garner and S. C. Wallwork, *Chem. Comm.*, 1969, 108; *J. Chem. Soc.* (*A*), 1970, 3092.

[13] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[14] D. W. Amos, Ph.D. Thesis, Nottingham, 1967.

[15] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, 1962, **36**, 324.

[16] G. S. Brownlee, Ph.D. Thesis, Nottingham, 1969.

[17] H. Brintzinger and R. E. Hester, *Inorg. Chem.*, 1966, **5**, 980.

[18] R. J. Fereday and D. Sutton, *Chem. Comm.*, 1966, 510.

[19] D. W. A. Sharp and J. Thorley, *J. Chem. Soc.*, 1963, 3557.

are undoubtedly due to gold–oxygen stretching and in each case only one component is observed.

TABLE 1

Infrared spectra (cm^{-1}) of tetranitratoaurates(III)

$HAu(NO_3)_4\cdot3H_2O$ [a]	$NaAu(NO_3)_4$ [a]	$KAu(NO_3)_4$ [a]	$RbAu(NO_3)_4$ [a]	$CsAu(NO_3)_4$ [a]	$NOAu(NO_3)_4$ [a]	$NOAu(NO_3)_4$ [b]	$NO_2Au(NO_3)_4$ [a]	$NO_2Au(NO_3)_4$ [b]	Assignment (C_s,NO_3)
3500—3000m,vb									H_2O or HNO_3
							2362vs,sp	2365s	$[\nu_{as}(NO_2^+)]$
							2345s,sp		
					2288m,sp	2290m,†			$[\nu(NO^+)]$
						1745m		1740w	N_2O_4
1680w,b						1680m,sh		1675s,sh	HNO_3
1560vs,b	1570vs,b	1570vs,b		1568vs,b	1560vs,b	1600sb †	1560vs,b	1600s,b †	$A'[\nu_{as}(NO_2)]$
				1548vs,sp		—1350		—1350	
1260vs,b	1265vs,b	1265vs,b		1305w,sh	1260vs,b	1310s	1260vs,b	1310s	$A'[\nu_s(NO_2)]$
				1286m,sh		1260vs		1260vs	
				1272m,sh					
				1268s,b					
				1250s,b					
915s,b	925vs,b	915vs,b	910vs,b	956w,sh	912vs,b	900vs,b †	910vs,b	900vs,b †	$A'[\nu_s(NO\ ^*)]$
				935m,sh					
				900s,b					
788w	800vw,sh	802s,sp	793sp	803vw,sp	798s,sp		798m,sp	795	$A''[\pi(NO_3)]$
	796w,sp	793m,sp		795w,sp	790sh		794sh		
770s,sp	772s,sp	772vs,sp	770vs,sp	780m,sp	770vs,sp	775m	768s,sp	775m	$A'[\delta_s(NO_2)]$
				770s,sp		750m		748m	
								732m	
718m,sp	718w,sh	719m	712sh	704m,sp	716m,sp	702w,sh	720m,sp	700m,sh	$A'[\delta_{as}(NO_2)]$
708m,sp	712m,sp	708s,sp	706vs,sp	691m,sp	705m,sp		705s,sp		
							590s,sp		$[\delta_d(NO_2^+)]$
							572vs,sp		
		378s,b		378s,b	378s,b		378b		$[\nu(Au–O)]$

[a] Solid. [b] Solution in $MeNO_2$.

* Co-ordinated oxygen. † Augmented by solvent absorption.

TABLE 2

Raman spectra (cm^{-1}) of tetranitratoaurates(III)

$KAu(NO_3)_4$ [a]	$KAu(NO_3)_4$ [b]	$CsAu(NO_3)_4$ [a]	$NO_2Au(NO_3)_4$ [a]	$NO_2Au(NO_3)_4$ [c]	$NOAu(NO_3)_4$ [a]	Assignment (C_s,NO_3)
					2300w,b	$[\nu(NO^+)]$
1588w	1585w (p)	1582w	1582w		1581w	$A'[\nu_{as}(NO_2)]$
1555w		1555w	1549w		1550w	
	1395w		1395w			$[\nu_s(NO_2^+)]$
1311s		1308s	1309s	1308w (p)	1310s	$A'[\nu_s(NO_2)]$
963s		948vw	950w		954vw	$A'[\nu_s(NO\ ^*)]$
925w		923vw	915vw			
784vs	780s (p)	784s	785s	775w (p)	786s	$A'[\delta_s(NO_2)]$
768s		774m,sh	763vs		768vs	
708w	704m (p)	712m	704w	708w	704w	$A'[\delta_{as}(NO_2)]$
698m		698w	692m		692m	
360vvs	358 (p)	360vvs	358vvs	357s (p)	358vvs	$[\nu(Au–O)]$
	266		230w			Lattice modes or skeletal deformations
	202					
187m			185m		187m	
160m			158m		157m	
			140w			
			119w			

[a] Solid. [b] Solution in 100% HNO_3. [c] Solution in $MeNO_2$.

* Co-ordinated oxygen.

(p) Polarised.

The isolation of tetranitratoaurate(III) salts has provided a useful opportunity to study the vibrational spectroscopic characteristics of the unidentate nitrate group in an environment free from steric influences of other ligands. In consequence, the present studies led to the development of what appears to be an unequivocal vibrational spectroscopic means of distinguishing between the possible modes of nitrate attachment in nitrato-complexes. (The bridging nitrate ligand, owing to lack of spectroscopic data and the paucity of authenticated examples of such species has not been included in these considerations.) Several such criteria have been proposed in recent years[20] but, in general, the presence of more than one nitrate group can lead to

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[20] (*a*) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222; (*b*) J. R. Ferraro, *J. Mol. Spectroscopy*, 1960, **4**, 99; (*c*) G. Topping, *Spectrochim. Acta*, 1965, **21**, 1743; (*d*) ref. 17 and R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, 1966, **5**, 1308.

great interpretive difficulties. However, the recent accumulation of Raman data has brought to light a further aspect of nitrate spectra which has, in all cases encountered so far, provided a reliable indication of the mode of co-ordination. This is to be found in the sequence of relative intensities of the three highest frequency Raman shifts attributable to N–O stretching fundamentals. The intensity sequence for unidentate species differs significantly from that of bidentate species. In summary, it has been found that for unidentate nitrato-groups, the bands at *ca.* 1300 cm^{-1} (NO_2 symmetric stretch) are generally fairly intense and by no means the least intense of the three high frequency N–O stretching fundamentals. In contrast, for bidentate species the bands at *ca.* 1300 cm^{-1} (now the NO_2 antisymmetric stretch) are weak and without exception, the least intense of the three.[13] In the spectra of solids containing $Au(NO_3)_4^-$ the 1300 cm^{-1} band is strong (Table 2). This qualitative criterion appears to work well in the absence of ligands other than nitrate, but there is an indication that it retains its empirical validity even in the presence of other co-ordinated groups, *e.g.* in the compound $Me_2Ge(NO_3)_2$.[21]

The presence of multiplets in the three regions of N–O stretching due to intramolecular coupling, which hinders the effective use of Raman polarisation data in ascertaining the mode of nitrate co-ordination, does not complicate the relative intensity considerations. In such cases, the ' envelopes ' of the component bands in each region provide the same unequivocal distinctions. Another advantage of the intensity criterion is that the relative intensity pattern for any particular compound appears to remain the same whether the data is collected from the solid or solution samples.

X-*Ray Powder Photographs*.—In all cases, the number of reflection lines observed for the alkali-metal tetranitratoaurate(III) salts was extremely large, and it proved impossible to index the photographs. Visual comparison of the photographs indicated no obvious isostructural relationship between any two members of the alkali-metal series, but it would be hazardous to conclude, on this basis alone, that in fact no two salts of the series were isostructural. The cell constants of the potassium salt are known from the single crystal study.[12] Using this data, it may be possible to obtain further information on the structures of the other alkali-metal tetranitratoaurates(III).

Electrical Conductivity.—A conductivity measurement on a freshly prepared solution of the nitronium salt in nitromethane (8×10^{-4}M) gave $\Lambda_M = 46{\cdot}6\ \Omega^{-1}\ cm^2$ at 0 °C, which is close to that expected for the dissociation in nitromethane of an (A^+B^-) electrolyte.[22] This is consistent with the vibrational spectra of these solutions, which supported the ionisation

$$NO_2^+[Au(NO_3)_4]^- \longrightarrow NO_2^+ + [Au(NO_3)_4]^-$$

in nitromethane. The value of Λ_M decreased almost linearly with time; this is also consistent with the solution spectra, which indicated that on slow decomposition the non-electrolyte N_2O_4 was formed.

The Existence of Anhydrous Gold(III) *Nitrate*.—The isolation of this compound has been previously claimed by Field and Hardy.[4] These workers treated ' hydrated gold(III) nitrate ' with ' liquid ' dinitrogen pentoxide. Subsequent evacuation and vacuum sublimation of the reaction mixture gave rise to a golden-yellow sublimate in small yield, which was assumed to be the anhydrous trinitrate on the basis of gold content only. Work in these laboratories has shown that ' liquid ' dinitrogen pentoxide generally produces nitronium tetranitratoaurate(III) in its reactions with gold and its compounds. Occasionally, the reagent contains a high proportion of dinitrogen tetroxide and in such cases has produced nitrosonium tetranitratoaurate(III) in preference to the usual nitronium salt. In our experience, neither of these compounds gives rise to anhydrous gold(III) nitrate on vacuum sublimation. The nitronium salt steadily evolves nitrogen oxides, producing gold(III) oxide which further decomposes to the metal at temperatures greater than 250°. However, the nitrosonium salt, upon vacuum sublimation at 80° (10^{-3} mm) whilst decomposing apparently in a similar manner to the nitronium salt, produces a very small amount of a highly reactive golden-yellow sublimate as a thin crust upon a cold-finger. This sublimate displays properties characteristic of nitronium tetranitratoaurate(III). A similar conversion has been noted previously in the vacuum sublimation of nitrosonium tetranitratoferrate(III).[23]

Hexanitratoaurates(III).—In the course of his studies on the complex acid $HAu(NO_3)_4,3H_2O$, Schottlander [2] reported that the addition of stoicheiometric proportions of potassium nitrate to nitric acid solutions of the complex acid yielded, on evaporation, a salt of composition $2KNO_3,HAu(NO_3)_4$, alternatively formulated as $K_2HAu(NO_3)_6$. We have found that the true constitution of this yellow, crystalline product is given by $KNO_3,KAu(NO_3)_4$ [Found: Au, 33·2; N, 12·2; K, 13·0. $K_2HAu(NO_3)_6$ requires Au, 30·4; N, 13·0; K, 12·0. $KNO_3,KAu(NO_3)_4$ requires Au, 33·6; N, 12·0; K, 13·3%. The ratio of gold to nitrate ion obtained from an alkaline hydrolysate of the complex was found to be 1 : 4·9. $K_2HAu(NO_3)_6$ requires 1 : 6, $KNO_3,KAu(NO_3)_4$ requires 1 : 5]. The i.r. spectrum of the product gave strong evidence for the presence of both ionic and covalent nitrate groups, thus supporting the double-salt formulation.

An attempt was made to prepare potassium hexanitratoaurate(III) by the stoicheiometric addition of potassium nitrate to nitric acid solutions of potassium tetranitratoaurate(III). The golden-yellow crystals which separate upon evaporation were found to display bands characteristic of both ionic and covalent nitrate in the i.r. spectrum. The ion $Au(NO_3)_6^{3-}$ appears

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[21] D. Potts and A. Walker, personal communication.

[22] J. Ferguson and R. S. Nyholm, *Nature*, 1958, **183**, 1039.

[23] C. C. Addison, P. M. Boorman, and N. Logan, *J. Chem. Soc.*, 1965, 4978.

reluctant to form under these conditions, and this is consistent with the preference of the gold(III) ion for four-co-ordinate stereochemistry.

Reactivity of the Unidentate Nitrate Group.—Compounds containing the unidentate nitrate group are generally unreactive towards aliphatic ethers and hydrocarbons, whereas those which contain bidentate groups generally possess strong oxidising and nitrating powers towards these compounds. The presence of symmetrically bidentate nitrate groups and a relatively accessible lower oxidation state for the metal appear to be essential to this high chemical reactivity and a mechanism involving the release of NO_3 radicals by such bidentate species has been proposed to explain this phenomenon.[24,25] The tetranitratoaurate(III) ion however, in the absence of the highly reactive NO_2^+ and NO^+ ions, is passive in hexane. It decomposes smoothly and mildly in diethyl ether but this could equally well be attributed to reduction of gold(III). It does react with some vigour in dimethyl sulphoxide and pyridine, but these solvents have high co-ordinative ability and conceivably compete strongly with the nitrate groups for a co-ordination site around the oxidising gold(III) centre. In general, the tetranitratoaurate(III) anion does not display the reactivity which has so far been considered typical of the bidentate nitrate group.

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