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Communications

The Tetranuclear Ruthenium(IV) Aqua Ion: Evidence in Support of Its Formulation as $H_n[Ru_4O_6(OH_2)_{12}]^{(4+n)+}$ (n = 0–4)

The precise molecular structure of the ruthenium(IV) cationic species present in noncomplexing acidic solutions remains unknown, despite an extensive series of published studies spanning four decades.[1] It is generally agreed that a tetranuclear species is relevant on the basis of electrochemical results (reduction to Ru(3.75) and Ru(3.25))[2–4] and oxidation to Ru(4.25)[5] oxidation states) and charge/metal determination using cation-exchange chromatography[4] coupled with Donnan membrane equilibrium[6] studies at pH 1–2 in $HClO_4$ solution. The structures proposed, $[Ru_4(OH)_{12}]^{4+}$ and $[Ru_4O_6]^{4+}$, seem consistent with the findings, with the former tending to be favored.[1] Reduction to give ultimately a tetranuclear Ru(III) ion, which decomposes in an $[H^+]$-independent first-order process to give a "dimeric" form, conceivably $[Ru_2(OH)_2]^{4+}$ or $[RuORu]^{4+}$, has been well documented[3,4] but offers no further insight into the nature of the Ru(IV) species involved.

Surprisingly no derivative complexes (replacement of coordinated water ligands) have been characterized in the hope of shedding light on the nature of the core structure. We, like others, have discovered that certain simple ligands do substitute into the Ru(IV) coordination sphere but lead to accompanied reduction to mononuclear[7] (NCS^-, $C_2O_4^{2-}$) and dinuclear[8] (Cl^-, Br^-) Ru(III) complexes. We believe that stable tetranuclear Ru(IV) complexes exist with ligands such as EDTA and MIDA ((methylimino)diacetate), but these complexes remain poorly characterized on the basis of elemental analysis.

We wish to report here significant progress in characterizing one such derivative complex isolated following the reaction of $Ru^{IV}(aq)$ with $K[HB(pz)_3]$[9] (pz = 1-pyrazolyl) at pH 2 in the presence of a number of counteranions, which has provided substantial evidence for its formation via simple substitution of the water ligands coordinated to the tetranuclear $Ru^{IV}(aq)$ core.

In the first instance, we sought to prepare samples of $Ru^{IV}(aq)$ enriched with ^{17}O in the hope of being able to elucidate the solution structure of the ion directly via ^{17}O NMR measurements because of the successful studies on the trinuclear $[M_3O_4(OH_2)_9]^{4+}$ ions (M = Mo, W).[10] Possible methods to ensure total enrichment with ^{17}O (to suitable levels ~5 atom %) were considered. The standard method for preparing $Ru^{IV}(aq)$ solutions, via treatment of RuO_4 with solutions of H_2O_2 in $HClO_4$,[11] was rejected because there was no guarantee that controlled enrichment of all oxygens in both intermediates and products could be achieved. Other preparative routes such as treatment of $[RuBr_6]^{2-}$ with BrO_3^- in $HClO_4$[12] were also rejected for similar reasons. In the end, it became clear that electrochemical oxidation[13] of fully exchanged $[Ru(OH_2)_6]^{2+}$[14] in HBF_4/H_2O[17] was the method of choice.

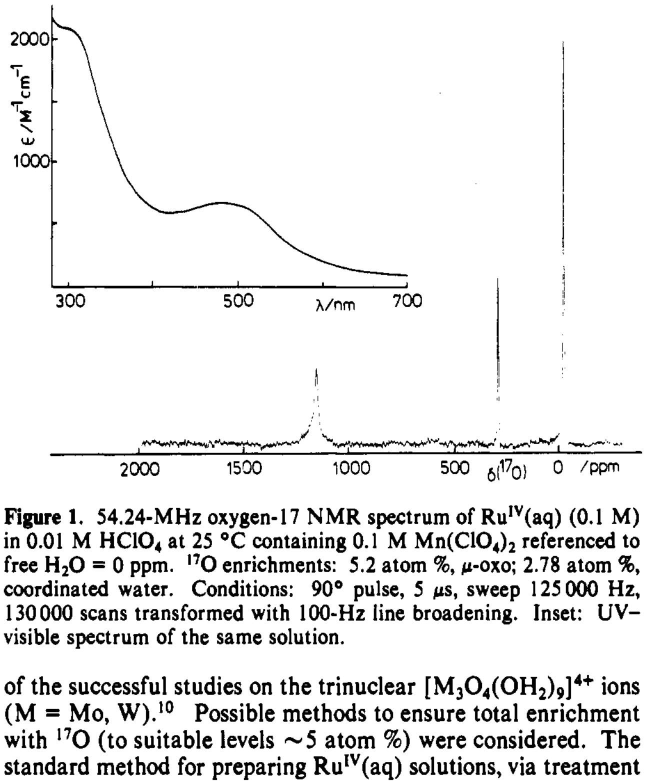

Figure 1. 54.24-MHz oxygen-17 NMR spectrum of $Ru^{IV}(aq)$ (0.1 M) in 0.01 M $HClO_4$ at 25 °C containing 0.1 M $Mn(ClO_4)_2$ referenced to free H_2O = 0 ppm. ^{17}O enrichments: 5.2 atom %, μ-oxo; 2.78 atom %, coordinated water. Conditions: 90° pulse, 5 μs, sweep 125 000 Hz, 130 000 scans transformed with 100-Hz line broadening. Inset: UV–visible spectrum of the same solution.

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(13) Electrochemical oxidation of $Ru^{2+}(aq)$ was carried out at constant current (0.5 A) with a simple galvanostatic setup employing a cylindrical platinum-gauze working electrode (area 6 cm^2) and a platinum-wire counter electrode in a one-compartment cell (volume 20 cm^3). The progress of the reaction was followed by UV–visible spectrophotometry until the peak of $Ru^{IV}(aq)$ at 487 nm reached a maximum. The oxidation proceeds via initial generation of yellow $Ru^{3+}(aq)$ and then probably mononuclear $Ru^{IV}(aq)$ prior to rapid condensation to give the tetranuclear unit in addition to higher polymeric species, detectable following subsequent ion-exchange separation.
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Table I

	elemental anal., %						selected FAB mass spectral data	
	calcd			found				
compound	C	H	N	C	H	N	*m/e*	assignment
$H_4[Ru_4O_6(HB(pz)_3)_4(Hpz)](NO_3)_4$	28.00	2.87	25.13	28.47	3.18	25.64	1423	$[^{102}Ru_4O_6(H^{11}B(pz)_3)_4(pz)]^{\bullet+}$
							1356	$[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet+}$
							678	$[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet 2+}$
							528	$[^{102}Ru(H^{11}B(pz)_3)_2]^{\bullet+}$
$H_4[Ru_4O_6(HB(pz)_3)_4(Hpz)](CF_3SO_3)_4\cdot 2H_2O$	25.10	2.53	17.71	24.75	2.65	18.15	1424	$[^{102}Ru_4O_6(H^{11}B(pz)_3)_4(Hpz)]^{\bullet+}$
							1356	$[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet+}$
							678	$[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet 2+}$
							528	$[^{102}Ru(H^{11}B(pz)_3)_2]^{\bullet+}$
$H_4[Ru_4O_6(HB(pz)_3)_4(Hpz)](ClO_4)_4$	25.19	2.58	19.59	25.85	2.64	20.35	1359[a]	$H_3[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet+}$
							679[a]	$H_2[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet 2+}$
$H_4[Ru_4O_6(HB(pz)_3)_4](ClO_4)_{1.5}(BPh_4)_{2.5}\cdot 4H_2O$	48.55	4.30	14.16	48.46	4.20	13.84	1360	$H_4[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet+}$
							678	$[^{102}Ru_4O_6(H^{11}B(pz)_3)_4]^{\bullet 2+}$
							528	$[^{102}Ru(H^{11}B(pz)_3)_2]^{\bullet+}$

[a] FAB MS data from sample found to contain no free pyrazole.

Solutions of $[Ru(^{17}OH_2)_6]^{2+}$ were prepared by reduction of RuO_4 in HBF_4 with Sn powder[15] followed by ion-exchange chromatography (Dowex 50W-X2) and treatment with samples of 10 atom % $H_2{}^{17}O$ (Yeda Co Ltd.). Following the electrochemical oxidation, ^{17}O-enriched samples of the Ru(IV) mixture were exchanged onto a column (5 cm × 1 cm) of Dowex 50W-X2 cation-exchange resin and the Ru(IV) aqua ion eluted with 0.25 M $La(ClO_4)_3$ in 0.01 M $HClO_4$, giving solutions ~0.05–0.1 M in Ru(IV) standardized at the peak maximum of 487 nm (ϵ = 709 M^{-1} cm^{-1} per Ru)[11] (Figure 1). Further $H_2{}^{17}O$ was then added to the eluates, resulting in the ^{17}O NMR spectrum (2 cm^3 of sample in a 10-mm tube) shown in Figure 1. Mn^{2+} (1 equiv/equiv of Ru) was also added in order to efficiently relax the bulk water signal[16] (referenced as 0 ppm). Three resonances were observed and assigned as follows: −24 ppm, coordinated water; 288 ppm, ClO_4^-; 1157 ppm, bridging oxygens. Unfortunately, an assignment of a definitive structure on the basis of the ^{17}O NMR spectrum was not possible in this case. However, variation in the level of enrichment at the −24 ppm resonance of the coordinated waters allowed a comparison of relative peak heights versus that of the nearby nonexchanging ClO_4^- counterion (natural abundance 0.037 atom %). This allowed an estimation of the number of coordinated waters per Ru as 3.1 ± 0.1. This result is immediately consistent with a number of possible tetranuclear structures one could consider, each having facial coordination of three waters on each Ru. Unfortunately, a similar quantitative assessment of the more remote bridging oxygen resonance was not possible. However, knowledge of the chemical shift (1157 ppm) proved useful in subsequent experiments.

In the absence of a definitive assignment of structure by ^{17}O NMR spectroscopy, the search for a characterizable solid derivative was maintained. In the end, a suitable complex was found by using the ligand hydridotris(1-pyrazolyl)borate; $HB(pz)_3^-$. Treatment of $Ru^{IV}(aq)$ at pH 2 with an excess of $K[HB(pz)_3]$ in the presence of various noncomplexing counterions led to precipitation of a red-brown microcrystalline powder in >70% yield. The isolation of crystalline samples suitable for X-ray diffraction studies has so far eluded us, but the results from elemental analyses and positive-ion fast-atom-bombardment (FAB) mass spectrometry on samples obtained from four different counterions are listed in Table I and illustrated for complexes with NO_3^- and ClO_4^- in Figure 2. With these latter two counterions, *m/e* clusters, consistent with the expected ruthenium and boron isotope patterns, were observed centered at *m/e* 1423 and 1356, corresponding to loss of a pyrazole (Hpz) from the molecular ion fragment, $[^{102}Ru_4O_6(H^{11}B(pz)_3)_4(Hpz)]^{\bullet+}$. It is not known whether the isolated pyrazole is coordinated or free in the complex. The presence of a coordinated free pyrazole, accompanied by bidentate ligation of two $HB(pz)_3^-$ ligands, has been observed in the structure of $[Mo_4S_4(HB(pz)_3)_4(pz)]$.[17]

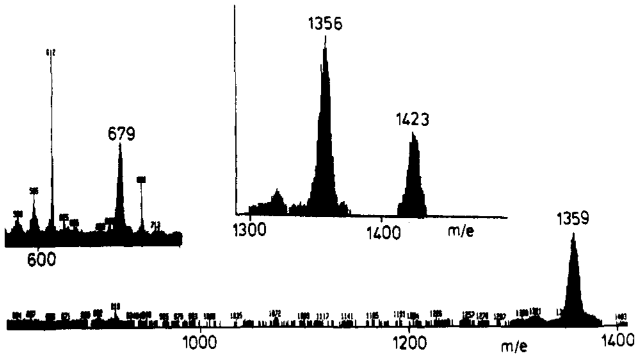

Figure 2. Positive-ion fast-atom-bombardment mass spectra of (left) $H_4[Ru_4O_6(HB(pz)_3)_4](ClO_4)_4$ and (inset) the NO_3^- salt (molecular ion region). Matrix: 3-nitrobutyric acid.

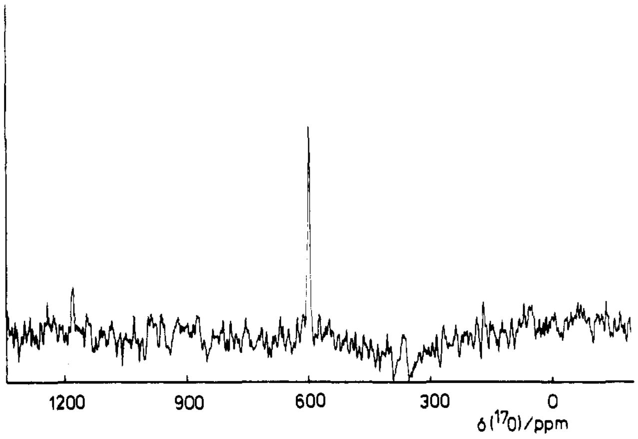

Figure 3. 40.56-MHz oxygen-17 NMR spectrum of 5% ^{17}O-enriched $H_4[Ru_4O_6(HB(pz)_3)_4](ClO_4)_4$ in acetonitrile (saturated solution) containing 10% acetone by volume.

The complexes isolated with $B(C_6H_5)_4^-$ and ClO_4^- counterions do not show the presence of an extra pyrazole; the highest *m/e* cluster fragment is now centered at 1359 or 1360. This observation appears to be consistent with protonation to give the cationic fragment relevant to the elemental analysis. Loss of H and/or X^- (the extent depending upon the nature of X^-) from the original ion pair is presumed responsible for the variation in the extent of protonation of the $[Ru_4O_6(HB(pz)_3)_4]^{\bullet+}$ fragment, a common phenomenon in FAB experiments.[18] A further feature of the FAB

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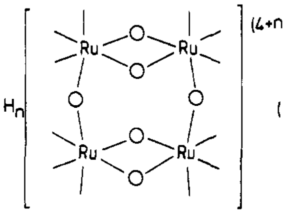
mass spectra (Figure 2) was the observation of half-mass peaks centered at $m/2e$ 678 (NO_3^-, $CF_3SO_3^-$, $B(C_6H_5)_4^-$) and 679 (ClO_4^-), corresponding to $m/2e$ fragments of variably protonated $[Ru_4O_6(HB(pz)_3)_4]^{\bullet 2+}$ ions. This is also a common phenomenon with polynuclear metal complexes.[18]

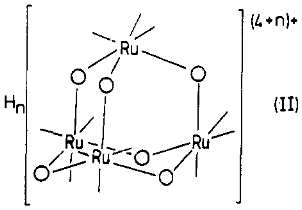
In order to verify whether the tetranuclear core structure found in the $HB(pz)_3^-$ complex was also representative of the aqua ion, an experiment linking the two together was needed. An ^{17}O-enriched sample of the complex was thus prepared and its ^{17}O NMR spectrum (saturated solution in CH_3CN, with acetone (+600 ppm vs H_2O) as internal reference) recorded (Figure 3). A weak but easily discernible resonance for the bridging oxygens was observed at ~1170 ppm, identical within experimental error with the chemical shift of the bridging oxygens of the aqua ion.

These results provide the first direct indication that the tetranuclear Ru(IV) aqua ion is a variably protonated $[Ru_4O_6(OH_2)_{12}]^{4+}$ unit, the extent of protonation depending upon $[H^+]$. The crucial observation was the existence of the fully deprotonated $Ru_4O_6^{4+}$-containing fragment in the FAB mass spectrum of the $HB(pz)_3^-$ complex with the NO_3^- or $CF_3SO_3^-$ counterion. A variable degree of positive charge on the aqua ion (depending upon $[H^+]$) is also implied from its ion-exchange behavior, displacement elution with e.g. La^{3+} at pH ≥1 being required. Attempts to elute the ion (on the basis of a presumed 4+ charge) with ≥1 M $HClO_4$ led to complete retention of the ion on the column. These observations imply that the protonation constants for formation of $H_4[Ru_4O_6(OH_2)_{12}]^{8+}$ lie somewhere in the range 10^{-2}–1 M.[19]

Two possible structures for $H_n[Ru_4O_6(OH_2)_{12}]^{(4+n)+}$ are shown in I and II. Structure I would seem more likely, given the observation that reduction to Ru(III) leads to depolymerization forming a dimeric product.[3] This could easily occur via cleavage of the Ru–O bonds linking the two $Ru(\mu_2\text{-}O)_2Ru$ units. Further protonation of the tetranuclear unit is known to accompany reduction to Ru(III),[3-5] and this may facilitate such bridge cleavage. On the other hand, the "adamantane-like" structure (II) accounts more easily for the appearance of only one bridging oxygen ^{17}O NMR resonance (closer analysis revealing no indication of two discernibly overlapping Lorentzian lines). We certainly believe, on the basis of the present results, that structures based on $[Ru_4(OH)_{12}]^{4+}$, favored by many workers,[1] can now be discounted.



(I)



(II)

(n = 0-4)

Support for the $Ru_4O_6^{4+}$ formulation also comes from the extensive Russian literature[20] with regard to reports of various green and brown Ru(IV) sulfato complexes obtained following heating of Ru(IV) chloro complexes in aqueous H_2SO_4 or following reduction of RuO_4 in the same medium. Ginzburg et al.[21] have formulated one of the brown complexes as $K_4H_6[Ru_4O_6(SO_4)_6]$ (Ru(3.5)) on the basis of thermal decomposition and on the basis of IR studies which appear to rule out the presence of μ-OH bridges. Similar Ru(IV) derivatives probably exist but remain poorly characterized. Efforts will continue to find a derivative providing suitable crystals for X-ray structural analysis.

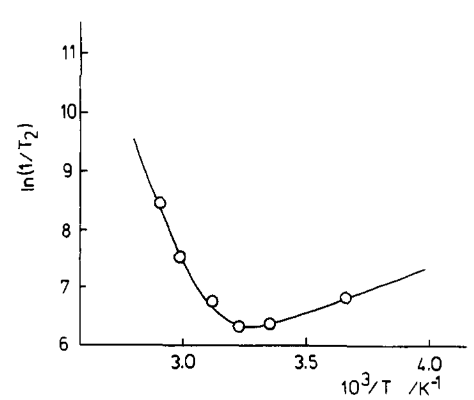


Figure 4. Temperature variation of the transverse relaxation time for the coordinated water resonance of 5% ^{17}O-enriched $Ru^{IV}(aq)$ (0.1 M) in 0.01 M $HClO_4$, μ = 1 M ($NaClO_4$). The line represents the fit to eq 1.[23]

Water exchange at the bridging oxygen atoms is extremely slow ($t_{1/2}$ >6 months at 25 °C), in support of their assignment. In contrast, water exchange at the coordinated water ligands is relatively fast and has been studied by dynamic measurement of the line width (T_2 relaxation time) of the −24 ppm ^{17}O NMR resonance as a function of temperature at pH 1, μ = 1 M ($NaClO_4$). The quadrupolar relaxation contribution (T_{2Q}) was determined by measurements of T_2 at temperatures below 30 °C, thus outside the kinetic exchange region. The resulting T_2 values (Figure 4) were fitted to the relationship (1)[22] as a function of

$$\ln(1/T_2) = \ln(1/T_{2Q}) + k_{ex} \qquad (1)$$

temperature by use of a nonlinear-least-squares treatment (weighting unity),[23] giving rise to $k_{ex}(25\ °C) = 29\ s^{-1}$, $\Delta H_{ex}^* = 85 \pm 16\ kJ\ mol^{-1}$, and $\Delta S_{ex}^* = +69 \pm 47\ J\ K^{-1}\ mol^{-1}$. Values of k_{ex} for Ru(IV) may now be compared to those observed[14] for the mononuclear aqua ions of Ru^{2+} and Ru^{3+}, showing variation over 7 orders of magnitude:

$$\begin{array}{lccc} & [Ru_4O_6]^{4+} > & [Ru(OH_2)_6]^{2+} > & [Ru(OH_2)_6]^{3+} \\ k_{ex}(25\ °C)/s^{-1} & \sim 10 & \sim 10^{-2} & \sim 10^{-6} \end{array} \qquad (2)$$

The presence of a trans-labilizing effect from the bridging μ_2-oxygens within the tetranuclear structure is presumed to play a role in the manifestation of the high lability shown by the water ligands in the Ru(IV) ion.

Acknowledgment. We express special thanks to Professor A. E. Merbach and Dr. L. Helm (University of Lausanne, Switzerland) both for providing facilities and for assistance with the ^{17}O NMR determination of the water exchange of the Ru(IV) ion using the Bruker AM-400 instrument. We also thank the SERC for the award of an earmarked studentship and a travel grant to Switzerland (A.P.) and for time on the positive-ion fast-atom-bombardment mass spectrometer at the University College of Swansea, Wales, U.K. Finally, we wish to thank

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(19) Retention of the tetranuclear structure during protonation is believed to be also supported by the lack of any gross changes either in the UV-visible spectrum or in the ^{17}O NMR spectrum (no loss of the μ-O peak) within the range of $[H^+]$ (10^{-2}–2 M) wherein the differing ion-exchange elution behavior is observed. As a result, protonation to give ultimately $H_4[Ru_4O_6(OH_2)_{12}]^{8+}$ below pH 2 accounts for the resulting Ru(IV) species detected previously having apparent charge/Ru = 2. This species, we believe, has been wrongly assigned[11] to "mononuclear" $Ru(OH)_2^{2+}$ or RuO^{2+} species. The lack of spectral changes also tends to rule out variable degrees of polymerization and/or precipitation of hydrous RuO_2 as being responsible for the differing ion-exchange behavior.

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(22) Martin, M. L.; Delpeuch, J.-J.; Martin, G. *Practical NMR Spectroscopy*; Heyden and Son Ltd.: London, 1980.

(23) The temperature variation of the transverse relaxation time was fitted by assuming an Arrhenius term for T_{2Q} and an Eyring relationship for k_{ex}. Line shapes were analyzed by using a program called ANAPHASE, and the entire fit of (1) to temperature was analyzed by using ITERAT. The nonlinear-least-squares programs were executed by using a Norsk Data processing system (560) on a VAX 8550 computer. Both ANAPHASE and ITERAT are programs developed at the ICMA, University of Lausanne, Switzerland.

Johnson Matthey plc for generous loans of ruthenium trichloride.

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Tertiary Amine Adducts of Gallane: Gallane-Rich [{GaH₃}₂(TMEDA)] (TMEDA = *N,N,N′,N′*-Tetramethylethylenediamine) and Thermally Robust [GaH₃(quinuclidine)]

There has been renewed interest in gallane with the synthesis of digallane, $H_2Ga(\mu\text{-}H)_2GaH_2$,[1] and gallaborane, $H_2Ga(\mu\text{-}H)_2BH_2$,[2] and the use of tertiary amine adducts of gallane in the presence of nitrogen for chemical vapor deposition of gallium nitride.[3] While gallane readily forms adducts with tertiary amines, only an imprecise structure of one of them, H_3GaNMe_3, has been studied in the solid,[4] possibly because of their tendency to decompose to gallium metal, amine, and hydrogen close to room temperature.[5]

Herein we report (i) the synthesis of some new gallane/tertiary amine adducts; (ii) studies on varying the nature of the amine, either the alkyl substituents on the amine or the number of tertiary amine centers/Lewis base, where the thermal stability of the adducts is affected and (iii) the first complete crystal structure determinations of gallane/tertiary amine adducts, viz the 2:1 gallane/TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) and 1:1 gallane/quinuclidine adducts.

Treatment of H_3GaNMe_3[6] with excess TMEDA in diethyl ether gave a 1:1 gallane/TMEDA adduct, $H_3Ga(TMEDA)$, as a white solid, which rapidly lost $^1/_2$ equiv of Lewis base in vacuo (weight loss), via a colorless oil, affording solid $[\{H_3Ga\}_2\{(NMe_2CH_2)_2\}]$ (**1**) in high yield. This and the synthesis of the quinuclidine adduct $[H_3Ga\{N(CH_2CH_2)_3CH\}]$ (**2**) are shown in Scheme I.[7] The instability of the 1:1 gallane/TMEDA adduct with respect to loss of one tertiary amine center/metal center is similar to that established for the gallane/bis(trimethylamine) adduct, which exists only between −45.4 and −22.8 °C, decomposing at higher temperatures to H_3GaNMe_3.[8] In contrast, the corresponding alane/bis(trimethylamine) can be purified as a crystalline solid in the presence of excess trimethylamine.[9] Furthermore, the 1:1 alane/TMEDA adduct is thermally stable, sublimable in vacuo without decomposition.[10]

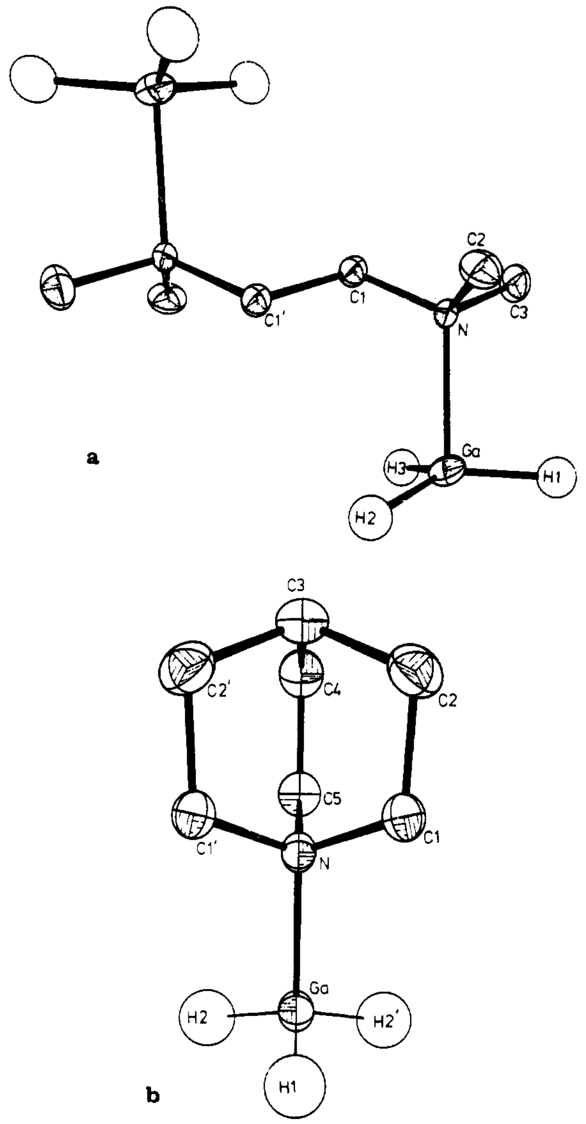

Figure 1. Molecular projections of (a) $[\{H_3Ga\}_2\{(NMe_2CH_2)_2\}]$ (**1**) and (b) $[H_3Ga\{N(CH_2CH_2)_3CH\}]$ (**2**) with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms shown. Bond distances [Å] and angles (deg) are as follows. Compound **1**: Ga–N = 2.094 (4), Ga–H(1,2,3) = 1.36, 1.40, 1.57, N–C(1) = 1.476 (7), N–C(2) = 1.481 (7), N–C(3) = 1.478 (7), C(1)–C(1)′ = 1.51 (1); N–Ga–H(1,2,3) = 103, 99, 97, H(1)–Ga–H(2,3) = 125, 114, H(2)–Ga–H(3) = 112, Ga–N–C(1,2,3) = 113.2 (3), 108.6 (4), 106.9 (4), C(1)–N–C(2,3) = 112.7(5), 106.6 (4), C(2)–N–C(3) = 108.5 (5), N–C(1)–C(1)′ = 113.8 (6). Compound **2**: Ga–N = 2.063 (4), Ga–H(1,2) = 1.69 (6), 1.55 (5), N–C(5) = 1.507 (6), C(1)–C(2) = 1.529 (5), C(2)–C(3) = 1.525 (5), C(3)–C(4) = 1.514 (7), C(4)–C(5) = 1.514 (7); N–Ga–H(1,2) = 100 (2), 105 (2), H(1)–Ga–H(2) = 117 (2), H(2)–Ga–H(2)′ = 110 (2), Ga–N–C(1,5) = 110.7 (2), 110.6 (3), C(1)–N–C(1)′ = 108.1 (3), C(1)–N–C(5) = 108.3 (3), N–C(1)–C(2) = 111.9 (3), C(1)–C(2)–C(3) = 108.7 (3), C(2)–C(3)–C(2)′ = 108.3 (3), C(2)–C(3)–C(4) = 109.1 (3), C(3)–C(4)–C(5) = 109.6 (4), N–C(5)–C(4) = 114.4 (4).

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(7) Compounds **1** and **2** were synthesised as follows. To synthesize **1**, a solution of TMEDA (1.3 mL, 8.64 mmol) in OEt_2 (5 mL) was added over 30 min to H_3GaNMe_3 (0.95 g, 7.20 mmol, prepared by a variation of the literature procedure)[6] in OEt_2 (15 mL) at 0 °C. After 1 h at room temperature, volatiles were removed in vacuo, to yield initially a white solid, then after 1 min a colourless oil followed by a white solid of **1** after 3–5 min. This was recrystallized as colorless prisms overnight at −20 °C from OEt_2 (15 mL) (0.88 g, 95% yield). Mp: 74–76 °C dec. ^1H NMR (300 MHz, toluene-d_8, 243 K): δ (relative to TMS) 1.49 (12 H, s, CH_3) 2.55 (4 H, s, CH_2), 4.78 (6 H, broad s, GaH_3); ^{13}C NMR (243 K): δ 46.64 (s, CH_3) 56.7 (s, CH_2). IR: ν_{Ga-H} 1840 cm^{-1}. To synthesize **2**, quinuclidine hydrochloride (1.96 g, 13.4 mmol) was added over 30 min to a solution of $Li[GaH_4]$ (1.08 g, 13.4 mmol, prepared by a variation of the literature procedure)[6] in OEt_2 (100 ml) at −80 °C, resulting in an immediate evolution of gas. After warming to room temperature, the mixture was stirred for 2 h and then filtered and the volatiles removedc in vacuo to yield a white solid. Sublimation of the resulting white solid (0.2 mmHg, 65–70 °C) afforded colorless prisms of **2** (2.32 g, 94% yield). Mp: 100–101 °C dec. ^1H NMR (250 MHz, C_6D_6): δ (relative to TMS) 0.93 (6 H, m, CH_2), 1.12 (1 H, m, CH) 2.60 (6 H, t, NCH_2) 4.80 (3 H, broad s, GaH_3); ^{13}C NMR, δ 19.26 (s, CH) 25.0 (s, CH_2) 48.87 (s, CH_2N). IR: ν_{Ga-H} 1810 cm^{-1}. Anal. Calcd for $C_7H_{16}GaN$: C, 45.7; H, 8.8; N, 7.6. Found: C, 46.1; H, 8.7; N, 7.7.

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