Pseudohalide Complexes of Trialkylgallium(III)

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Trimethyl- and triethyl-gallium(III) react with NMe_4X (X = CN, NCO, NCS, and N_3) to form well defined complexes of general formula $NMe_4[R_3GaX]$ (R = Me or Et) and, with the exception of X = NCO and NCS, $NMe_4[(R_3Ga)_2X]$. From i.r. and Raman spectra, it can be deduced that in the 1 : 1 [gallium(III) : pseudohalide] cyano-, cyanato-, and thiocyanato-complexes metal–pseudohalide bonding occurs between the gallium and carbon, the gallium and nitrogen, and the gallium and sulphur atoms respectively. The bonding between gallium and the cyanide ligand in the 2 : 1 complexes occurs through both the carbon and nitrogen atoms, whereas in the analogous azido-complexes, pseudohalide bonding to the metal occurs only through the α-nitrogen atoms.

THE ability of various pseudohalogen groups to function as bridging ligands in organometallic complexes has been frequently reported. Thus dialkylgold(III) cyano-complexes have tetrameric structures $[R_2AuCN]_4$,[1] the diethylmetal thiocyanato-complexes of aluminium(III), gallium(III), and indium(III) exist as the trimeric species $[R_2GaSCN]_3$ with the sulphur atoms of the SCN groups acting as bridges between the metal atoms,[2] and the analogous dialkylmetal azido-complexes are also trimeric, the α-nitrogen atoms of the azido-groups forming, with the metal atoms, planar six-membered rings.[3,4] The free pseudohalide ions can also form definite addition complexes with some alkylmetal complexes. Thus in the reactions of trimethylaluminium(III) and diethylberyllium(II) with CN^-, SCN^-, $SeCN^-$, and N_3^-, the following complexes have been isolated and in some cases characterised using vibrational spectroscopic techniques: $NMe_4[(Me_3Al)_2CN]$;[5] $NMe_4[(Me_3Al)_2XCN]$ (X = S or Se);[5] $K[(Me_3Al)_2SCN]$;[6] $NMe_4[Me_3AlSCN]$;[5] $NMe_4[(Me_3Al)_2N_3]$;[7] $NMe_4[Me_3AlN_3]$;[7] $NMe_4[(Et_2Be)_2SCN]$;[8] and $K[(Et_2Be)_4CN]$.[9] The crystal structure of the complex $K[(Me_3Al)_2N_3]$ has also been reported recently.[10] In the present work we describe complex formation between trialkylgallium(III) complexes and some tetramethylammonium pseudohalide salts. The tetramethylammonium cation was chosen on account of the favourable cation:complex anion size ratio.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen gas in a closed high-vacuum system. The salt NMe_4NCO was prepared from NMe_4Cl using KNCO-treated Amberlite 410 ion-exchange resin. After removal of water under vacuum, the raw product was recrystallised from isopropyl alcohol. Literature methods were used for the preparation of NMe_4CN,[5] NMe_4SCN,[11] NMe_4N_3,[7] and $GaEt_3$.[12] $GaMe_3$ and further samples of $GaEt_3$ were kindly provided by Dr. R. Dötzer, Siemens-Schuckertwerke A.G., Erlangen.

The complexes were prepared by two methods of which the following examples are typical.

(*a*) $NMe_4[(Me_3Ga)_2CN]$. A five-fold excess of $GaMe_3$ (2·90 g) was distilled on to finely powdered NMe_4CN (0·50 g), which had previously been thoroughly dried under high vacuum. After admission of nitrogen, the mixture was heated at 85 °C for some time, during which the complex formed as colourless crystalline *plates*. The excess of $GaMe_3$ was then pumped off until constant weight (1·63 g) was achieved.

(*b*) $NMe_4[Me_3GaCN]$. The complex $NMe_4[(Me_3Ga)_2CN]$ (0·48 g) was heated (2 h) at 120 °C under a dynamic vacuum. The product was a white *powder* (0·31 g). A summary of the preparative details together with the melting points and analytical data of the complexes is presented in Table 1.

I.r. spectra of solid samples were recorded, as Nujol and Hostaflon mulls mounted between caesium iodide plates, with a Perkin-Elmer 225 spectrometer. No exchange between the plates and the samples was observed. The Raman spectra were obtained with a Coderg PH 1 spectrometer using the 6328 Å line of a helium–neon laser and the 5145 Å line of an argon laser.

RESULTS AND DISCUSSION

Trimethyl- and triethyl-gallium(III) react with the anhydrous salts NMe_4X (X = CN or N_3) at room temperature or above according to equation (1) (R = Me or Et). In contrast are the reactions with NMe_4OCN and NMe_4SCN, where even the addition of a large excess of trialkylgallium(III) results in formation of the 1 : 1 complex only [equation (2); R = Me or Et, Y = OCN or SCN]. This behaviour should be compared with that of trialkylaluminium(III) complexes.[5,7,13] The stronger acceptor properties of the latter are shown by the ready formation of the complex $NMe_4[(Me_3Al)_2SCN]$ from $AlMe_3$ and NMe_4SCN. Treatment of $AlMe_3$ with cyanate ion leads to a violent reaction and rearrangement

$$2GaR_3 + NMe_4X \longrightarrow NMe_4[(R_3Ga)_2X] \quad (1)$$

$$GaR_3 + NMe_4Y \longrightarrow NMe_4[R_3GaY] \quad (2)$$

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[2] K. Dehnicke, *Angew. Chem.*, 1967, **79**, 942.

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[6] J. L. Atwood, P. A. Milton, and S. K. Seale, *J. Organometallic Chem.*, 1971, **28**, C29.

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[10] J. L. Atwood and W. R. Newberry, III, *J. Organometallic Chem.*, 1972, **42**, C77.

[11] C. R. McGrosky, F. W. Bergstrom, and G. Waitkins, *J. Amer. Chem. Soc.*, 1940, **62**, 2031.

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[13] F. Weller, I. L. Wilson, and K. Dehnicke, *J. Organometallic Chem.*, 1971, **30**, C1.

of the molecules in an, as yet, unknown manner. This can presumably be attributed to the stronger polarity of aluminium–carbon bonds compared with gallium–carbon bonds.

The cyano-complexes $NMe_4[(R_3Ga)_2CN]$ (R = Me or Et) decompose at 120 °C, whereby one trialkylgallium(III) molecule and the 1 : 1 complex are formed.

$$NMe_4[(R_3Ga)_2CN] \longrightarrow NMe_4[R_3GaCN] + GaR_3 \quad (3)$$

Both GaR_3 molecules are however lost from the 2 : 1 gallium(III) : azide complexes under these conditions. A possible explanation is that the expected 1 : 1 complex is in fact formed and then disproportionates into NMe_4N_3 and the 2 : 1 complex. This would be in agreement with our observations on the product formed by the reaction

$$2NMe_4[R_3GaN_3] \longrightarrow NMe_4[(R_3Ga)_2N_3] + NMe_4N_3 \quad (4)$$

of equimolar amounts of $GaEt_3$ and NMe_4N_3. A homogeneous crystalline product formed, which melted at 17 °C. The i.r. spectrum of the melt (see Table 4) showed bands characteristic of the products of reaction (4).

TABLE 1

Melting points, analytical data (%), and preparative details of the complexes

Complex	M.p. (t/°C)	Found (calc.) Ga	C	H	N	S	Preparative method; t/°C
$NMe_4[Me_3GaCN]$	194	32·5(32·4)	44·9(44·9)	9·8(9·8)	13·2(13·0)		(*b*); 120
$NMe_4[Et_3GaCN]$	47—48	27·8(27·1)	51·1(51·3)	10·4(10·5)	10·9(10·9)		(*b*); 120
$NMe_4[(Me_3Ga)_2CN]$	141—142	41·9(42·4)	39·9(40·2)	9·1(9·2)	8·7(8·5)		(*a*); 85
$NMe_4[(Et_3Ga)_2CN]$	*	33·0(33·4)	49·5(49·3)	10·2(10·2)	6·9(6·8)		(*a*); 90
$NMe_4[Me_3GaNCO]$	147—154	30·2(30·2)	41·3(41·5)	9·3(9·1)	12·0(12·1)		(*a*); 25
$NMe_4[Et_3GaNCO]$	33—36	25·4(25·6)	48·1(48·3)	9·7(9·9)	10·2(10·3)		(*a*); 25
$NMe_4[Me_3GaSCN]$ †	92—94	26·0(28·2)	39·0(38·8)	8·7(8·5)	11·4(11·3)	12·7(13·0)	(*a*); 25
$NMe_4[Et_3GaSCN]$	55—56	24·2(24·1)	45·5(45·7)	9·3(9·4)	9·9(9·7)	11·0(11·)1	(*a*); 40
$NMe_4[Me_3GaN_3]$	132—134	29·6(30·1)	36·4(36·3)	9·0(9·1)	24·1(24·2)		(*a*); 145 ‡
$NMe_4[Et_3GaN_3]$	17						(*a*); 25 ‡
$NMe_4[(Me_3Ga)_2N_3]$	87—89	40·1(40·3)	34·5(34·9)	8·5(8·7)	16·0(16·2)		(*a*); 25
$NMe_4[(Et_3Ga)_2N_3]$	38—39	32·3(32·5)	44·5(44·8)	9·8(9·8)	12·9(13·1)		(*a*); 25

* Forms a glass on cooling. † Not isolated free of NMe_4SCN. ‡ Mole ratio $NMe_4N_3 : GaR_3 = 1 : 1$.

TABLE 2

Principal bands in the vibrational spectra of the complexes $NMe_4[(R_3Ga)_2CN]$ and $NMe_4[R_3GaCN]$ (R = Me or Et)

$NMe_4[(Me_3Ga)_2CN]$ I.r.	Raman	$NMe_4[(Et_3Ga)_2CN]$ I.r.	Raman *	$NMe_4[Me_3GaCN]$ I.r.	Raman	$NMe_4[Et_3GaCN]$ I.r.	Raman	Assignment
2175s	2155s	2156s 2126vw,sh	2160s,p′ 2126mw,p	2135w	2137s	2124m	2125m	ν(C≡N)
541vs	546s	521vs	522s,dp	531vs	536s	517vs	523s	$\nu_{asym}(GaC_3)$
513m	591vs	497sh	497vs,p	513m	518vs	495sh	498vs	$\nu_{sym}(GaC_3)$
351s		365vs	372w,dp	325s	322m	311s		ν(Ga–CN)

* Liquid sample: p = polarised; p′ = partially polarised; and dp = depolarised.

All the complexes are hygroscopic and oxygen-sensitive, although considerably less so than free trialkylgallium(III). They are all wholly or partly soluble in an excess of the trialkylgallium(III) complex. The complexes of $GaMe_3$ are generally somewhat more stable than those of $GaEt_3$. Thus the complexes $NMe_4[(Et_3Ga)_2CN]$ and $NMe_4[(Et_3Ga)_2N_3]$ showed, at room temperature, a tendency towards dissociation which could be seen in the appearance in the vibrational spectra of relatively weak characteristic bands of the 1 : 1 complexes $NMe_4[Et_3GaCN]$ and $NMe_4[Et_3GaN_3]$ (see Tables 2 and 4).

The Vibrational Spectra of the Complexes.—$NMe_4[(R_3Ga)_2CN]$ *and* $NMe_4[R_3GaCN]$ (R = Me or Et). Vibrational spectra of these complexes are shown in Table 2. For the 1 : 1 complexes CN stretching vibrations were found at 2136 (R = Me) and 2125 cm^{-1} (R = Et). This suggests that the anion is in the cyano-, $[R_3GaC{\equiv}N{:}]^-$, rather than the isocyano-form, when comparison is made with the isoelectronic trialkylgermanium(IV) cyano-complexes, $[R_3GeCN]$, for which the CN stretching mode is observed [14] at 2197 cm^{-1}. The shift to lower frequency observed in the gallium complexes can be attributed to the negative charge of the anion. Evidence for an isocyano-molecule, $[R_3Ga{-}N{=}C]^-$, analogous to $[R_3GeNC]$, which is shown to be in equilibrium with $[R_3GeCN]$ through appearance in the i.r. spectrum [14] of a second band at 2100 cm^{-1}, could not be found. The spectrum of such a complex ion could be expected to contain an absorption band at *ca.* 2035 cm^{-1}. The addition of a second trialkylgallium(III) molecule resulted in a shift of the CN stretching vibration to 2156 (R = Me) and 2158 cm^{-1} (R = Et). This is in agreement with measurements made on the complexes $R_3Ge{-}C{\equiv}N \longrightarrow BF_3$ [14] and $MeC{\equiv}N \longrightarrow BF_3$ [15] in which complex formation leads to an increase of 50—100 cm^{-1} in this frequency.

The addition of a cyanide ion to the planar molecules

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[14] D. Seyferth and N. Kahlen, *J. Org. Chem.*, 1960, **25**, 809.

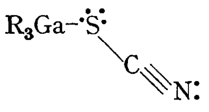
[15] H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

$GaMe_3$ (symmetry D_{3h})[16] and $GaEt_3$ (symmetry C_{3h})[17] results in a lowering of the local symmetry to at least C_{3v}, which must lead to the appearance of two GaC_3 stretching vibrations (E and A_1) both of which are i.r.- and Raman-active. This was observed for all the complexes. In $NMe_4[Me_3GaCN]$ for example, $\nu_{sym}(GaC_3)(A_1)$ occurs at 518 cm^{-1} and $\nu_{asym}(GaC_3)(E)$ at 536 cm^{-1}. The expected shift to lower frequency is shown clearly by comparison with $GaMe_3$, in which $\nu_{sym}(GaC_3)(A_1')$ lies at 522 cm^{-1} and $\nu_{asym}(GaC_3)(E')$ at 570 cm^{-1}.

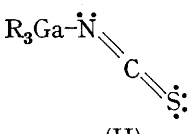
The Ga–CN stretching vibrations were observed at considerably lower frequencies, which may be partly due to the larger mass of the CN group. This absorption is found for the 1 : 1 complexes at 322 (R = Me) and 311 cm^{-1} (R = Et). The 2 : 1 complexes absorb at noticeably higher frequencies than their 1 : 1 analogues, at 351 and 368 cm^{-1} respectively. On account of the relatively high pseudosymmetry of the $[R_3Ga\text{–}C{\equiv}N\text{→}GaR_3]^-$ unit and the high intensity of this band in the i.r. spectrum, this band must be assigned to an unsymmetrically opposed vibration of the type $\overset{\rightarrow}{\mathrm{Ga}}\text{–}\overset{\leftarrow}{\mathrm{C}}{\equiv}\overset{\leftarrow}{\mathrm{N}}\text{–}\overset{\rightarrow}{\mathrm{Ga}}$.

$NMe_4[R_3GaNCO]$ *and* $NMe_4[R_3GaSCN]$ (R = Me or Et). Vibrational spectra of these complexes are shown in Table 3. The asymmetric and symmetric stretching vibrations of the NCO group, which occurred at *ca.* 2200 and 1330 cm^{-1} respectively, are completely in agreement with a nitrogen-bonded cyanato-group.[18] The correct assignment of these bands can be confirmed by a study of the combination modes at 3527 (R = Me) and 3513 cm^{-1} (R = Et). Because of the negative charge of the anion, stretching vibrations are found at lower frequencies than those of the isoelectronic germanium complexes prepared by Thayer *et al.* (2240 and 1415 cm^{-1} respectively).[19] The $[R_3Ga\text{–}NCO]^-$ structure is also suggested by the i.r. bands at 318 (R = Me) and 292 cm^{-1} (R = Et) which are assigned to the Ga–N stretching vibration. They are thus in the same region as the Ga–N stretching vibrations of the $[R_3Ga\text{–}N_3]^-$ ions (see below). They occur however at considerably lower frequency than the ν(Ge–N) vibration[19] of $[Me_3GeNCO]$ which lies at 454 cm^{-1}. The negative charge of the anion is again regarded as the explanation, this resulting in a strong polarisation of the gallium–pseudohalide bond.

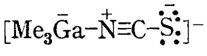
Complexing of the thiocyanate anion to the trialkylgallium(III) complex could occur through either the sulphur or the nitrogen atom, resulting in structures (I) and (II) respectively. Sulphur-bonded complexes are normally characterised by a relatively high ν(CN) (2050—2150 cm^{-1}) and a relatively low ν(CS) frequency (700—800 cm^{-1}), compared with those that bond through nitrogen[20] where ν(CN) lies in the region 1950—2080 cm^{-1} and ν(CS) 800—950 cm^{-1}. Exceptions do occur however since the position of these bonds can also be influenced by the mass of the atom bonded to the SCN group. The influence of the negative charge of the gallium complex must also be considered. In a nitrogen-bonded complex, this would encourage structures such as (III) which would be expected to cause a shift of ν(CN) to higher, and ν(CS) to lower, frequencies. The effect of the negative charge in a sulphur-bonded complex, however, would be to promote the structure (IV) leading to a decrease in ν(CN) and an increase in ν(CS).



(I)

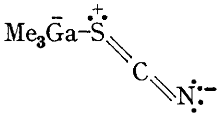


(II)



$$[\mathrm{Me_3}\overset{-}{\mathrm{Ga}}\text{–}\overset{+}{\mathrm{N}}{\equiv}\mathrm{C}\text{–}\overset{-}{\mathrm{S}}\mathrm{:}]^-$$

(III)



(IV)

In the spectrum of the complex $[Me_3Ga(SCN)]^-$ we observed ν(CN) at 2088 cm^{-1} and ν(CS) at 808 cm^{-1}. On comparing these values with those of the isoelec-

TABLE 3

Principal bands in the vibrational spectra of the complexes $NMe_4[R_3GaX]$ (R = Me or Et; X = NCO or SCN)

$NMe_4[Me_3GaNCO]$		$NMe_4[Et_3GaNCO]$		$NMe_4[Me_3GaSCN]$		$NMe_4[Et_3GaSCN]$		
I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	Assignment
3527w		3513w						$\nu_{sym}(NCO) + \nu_{asym}(NCO)$
2200vs	2209w	2198vs	2192vw					$\nu_{asym}(NCO)$
				2089vs	2089vs	2065vs	2078vs	$\nu(C{\equiv}N)$
1337w	1335m	1326m	1327m					$\nu_{sym}(NCO)$
				808vw	808m	804w	805m	ν(C–S)
621m	625vw	622s	626vw					δ(NCO)
531vs	536s	518s	522s	537vs	540s	523vs	526s	$\nu_{asym}(GaC_3)$
509m	513vs	495sh	490vs	514m	515vs	492m	494vs	$\nu_{sym}(GaC_3)$
				476w		477w		δ(SCN)
318s		292s						ν(Ga–N)
				236m		238m		ν(Ga–S)

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[16] J. R. Hall, L. A. Woodward, and E. A. V. Ebsworth, *Spectrochim. Acta*, 1964, **20**, 1249; G. E. Coates and A. J. Downs, *J. Chem. Soc.*, 1964, 3353.

[17] J. Chouteau, G. Davidovics, F. d'Amato, L. Savidan, and J. Lecomte, *Compt. rend.*, 1965, **260**, 2759.

[18] J. S. Thayer and R. West, *Adv. Organometallic Chem.*, 1967, **5**, 169.

[19] J. S. Thayer and D. P. Strommen, *J. Organometallic Chem.*, 1966, **5**, 383.

[20] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970.

tronic [$Me_3Ge(NCS)$] (2075 and 892 cm^{-1}),[19] which is known to exist as the isothiocyanato-form, it is clear that no definite structure assignment can be made. We believe, however, that the position of the metal–pseudohalide stretching mode (236—238 cm^{-1}) can be taken as evidence for the sulphur-bonded structure (I). In none of the other gallium–pseudohalide complexes is this vibration found at such low frequency, although ν(Ga–Cl)[21] in the anion [Me_3GaCl]$^-$, in which similar masses are involved, lies at 242 cm^{-1}.

TABLE 4

Vibrational spectra of the complexes $NMe_4[(R_3Ga)_2N_3]$ and $NMe_4[R_3GaN_3]$ (R = Me or Et)

$NMe_4[(Me_3Ga)_2N_3]$		$NMe_4[(Et_3Ga)_2N_3]$		$NMe_4[Me_3GaN_3]$		$NMe_4[Et_3GaN_3]$	
I.r.	Raman	I.r.	Raman [a]	I.r.	Raman	I.r.	Assignment
		3400w					
		3355w		3367m		3357m [b]	$\nu_{sym}(N_3)$ + $\nu_{asym}(N_3)$
						3325vw	
3337m		3328w		3327m		3291w [c]	
3031w	3032m	3028m	3030m,dp	3030m	3029m	3022m	[ν_{asym}(Me)]
	2974m		2975m,p		2974m		$\nu(CH_2)$, ν(Me)
	2948w		2948vw		2952sh		
2932s	2921w	2925vs	2919m,p′	2926s	2921m	2932vs	
2900sh	2902m			2905sh	2898m		
	2864w	2883vs	2881s			2900vs	
2847sh		2849vs	2853m	2841m	2849vw	2864vs	
		2799m	2806w,p			2810w	
		2710w	2709vw			2717vw	
		2630vw					
		2579vw		2581vw			
2546vw		2540vw					
2483vw		2475vw					
2323w				2340vw			
2079vs	2080vw	2073vs	2080w	2040vs	2060vw	2067s [b]	$\nu_{asym}(N_3)$
		2052				2010vs	
1483vs		1482vs		1479vs		1486vs	[δ_{asym}(Me)]
	1448m	1465sh	1454s,dp		1457w	1461sh	δ_{asym}(Me), [δ_{asym}(Me)]
1416w		1416m	1420m,dp	1416m		1415m	$\delta_{asym}(CH_2)$, [δ_{sym}(Me)]
		1368m	1366m,p′			1371m	δ_{sym}(Me)
		1341w		1344s [d]	1350w	1341m	
					1318vw		
1281s	1283m	1280s	1287m,p	1294s [d]		1286m	$\nu_{sym}(N_3)$, [ρ(Me)]
		1230m				1229m	$\delta(CH_2)$
1176s	1179s	1179m	1181s,p′	1175vs	1185m		$\omega(CH_2)$
		1105w				1105m	
		1055w				1066m	
		987s	994m,dp			998s	ν(C–C), $\tau(CH_2)$
946vs	944m	942vs	949m,p′	944vs	955w	946vs	$\nu_{asym}(NC_4)$
		920sh		915sh		925sh	ν(C–C), [$2\delta(NC_4)$]
	750m		751m,p		755m		[$\nu_{sym}(NC_4)$]
725vs				719vs			ρ(Me)
						690mw [b]	
690s		686m		659m			$\delta(N_3)$
		641s				648m,	$\rho(CH_2)$, $\gamma(N_3)$
						641w,[b]	
						630w [c]	
602w				612w			$\gamma(N_3)$
						560s	
541vs	541s	521s	528s,dp	533vs	537vs	515m	$\nu_{asym}(GaC_3)$
513m	514vs	489w	495vs,p	508w	510vs		$\nu_{sym}(GaC_3)$
		450vw	462vw,dp	453vw			[$\delta(NC_4)$]
			371vw				
343vs		341s		324vs			ν(Ga–N)
		287s					δ(CCGa), δ(CGaC), δ(CGaN)
		256s	264w,p				
238m				227w			
	199m		202vw		203s		
	172m				180w		
	125m						

The assignments in brackets are those of the NMe_4^+ cation, based on refs. 23 and 24.

[a] Liquid sample: p = polarised; p′ = partially polarised; and dp = depolarised. [b] Bands assigned to the complex $NMe_4[(Et_3Ga)_2N_3]$. [c] Bands assigned to the salt NMe_4N_3. [d] Fermi resonance (see text).

Further details of the vibrational spectra of the complexes $NMe_4[(R_3Ga)_2CN]$, $NMe_4[R_3GaCN]$, $NMe_4[R_3GaNCO]$, and $NMe_4[R_3GaSCN]$ (R = Me or Et) are to be found in Supplementary Publication No. SUP 20712 (7 pp., 1 microfiche).*

$NMe_4[(R_3Ga)_2N_3]$ *and* $NMe_4[R_3GaN_3]$ (R = Me or Et).

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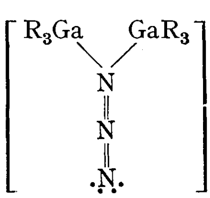
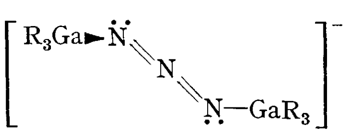
* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[21] K. Dehnicke and I. L. Wilson, unpublished work.

Vibrational spectra of these complexes are shown in Table 4. The positions of the characteristic stretching vibrations of the azido-group (ν_{asym} *ca.* 2060, ν_{sym} *ca.* 1280 cm^{-1}), together with the appearance in the i.r. spectrum of the symmetrical stretching mode, clearly show that these complexes contain homopolar gallium–azide bonds. The frequency changes compared with NMe_4N_3 [22] agree completely with expectation. The assignment of the band due to the symmetrical N_3 stretching vibration can be confirmed by a study of the combination ($\nu_{asym} + \nu_{sym}$) bands in the 3300 cm^{-1} region. Two combination bands at 3327 and 3367 cm^{-1} respectively appeared in the spectrum of the complex $NMe_4[Me_3GaN_3]$. These can be attributed to Fermi resonance involving the symmetrical N_3 stretching vibration and the first overtone of the azide deformation mode at 659 cm^{-1}. This leads to the appearance of two equally intense bands at 1294 and 1344 cm^{-1}.

For the complexes $NMe_4[(R_3Ga)_2N_3]$ the structures (V) and (VI) can be considered. The appearance in the i.r. spectra of strong $\nu_{sym}(N_3)$ bands is suggested as evidence for structure (V). Only a very small alteration of the dipole moment would be caused by this vibration in the case of structure (VI), resulting in a weak band. Furthermore, the fully polarised lines that are observed in the Raman spectrum of the complex $NMe_4[(Et_3Ga)_2N_3]$ would not be allowed by the C_2 symmetry of structure (VI). Symmetries C_{2v} (planar arrangement of the Ga_2NNN skeleton) and C_s (non-planar skeleton) are possible for structure (V). Since the selection rules do not allow fully polarised lines to arise in the Raman spectrum of a complex with C_s symmetry (classes A' partially polarised, A'' depolarised), the appearance of such lines immediately excludes this possibility and at the same time confirms the structure with C_{2v} symmetry. Although the partial polarisation which is also observed is not consistent with a C_{2v} structure, we suggest that it arises through accidental degeneracy of polarised and non-polarised lines. {In the related complex $K[(Me_3Al)_2N_3]$, it has been shown in an *X*-ray crystal-structure determination [10] that both aluminium atoms are bound to the α-nitrogen atom of the azido-group. A planar M_2N_3 skeleton is also found.}


(V)


(VI)

The gallium–nitrogen stretching vibrations, which were observed only in the i.r. spectra, can be clearly assigned to the bands at 343, 341, and 324 cm^{-1} respectively. The comparison with $[Me_3GeN_3]$,[19] whereby ν(Ge–N) lies at 456 cm^{-1}, again shows the large shift to lower frequency arising from the negative charge.

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