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BIS(DIALKYLMETAL)-*N*,*N*'-DIMETHYLOXAMIDES OF ALUMINIUM, GALLIUM AND INDIUM, PREPARATION, PHYSICAL AND SPECTROSCOPIC PROPERTIES

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Summary

The reaction of *N*,*N*'-dimethyloxamide with trialkyl derivatives of aluminium, gallium, and indium yields bis(dialkylmetal) compounds of structural formula $(R_2M)_2[O_2C_2(NCH_3)_2]$ (M = Al, Ga, In; and $R = CH_3, C_2H_5$). The $M_2O_2C_2N_2$ skeleton of these monomeric products forms an almost planar system of two fused five-membered rings, with S_2 symmetry. For the dimethylgallium and dimethylindium derivatives, ^1H and ^{13}C NMR spectra show the presence of two conformational isomers which differ in the orientation of the *N*-methyl relative to the two metal-bound CH_3 groups.

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1. Introduction

With dibasic acids H_2X, i.e. H_2SO_4, $H_2C_2O_4$, $H_2C_4O_4$, etc. [1-3], the simple trialkyls of aluminium, gallium, indium, or thallium form bis(dialkylmetal) derivatives of the acids. The reaction proceeds until completion according to eqn. 1.

$$2R_3M + H_2X \rightarrow (R_2M)_2(X) + 2RH \qquad (1)$$

Except for the aluminium compounds, the products are ionic in nature; thus, they may be dissolved in water without decomposition, dissociating into hydrated dialkylmetal cations, R_2M^+, and ligand anions, X^{2-}.

The *N*,*N*'-dimethyloxamide derivatives reported here can be thought of as derived from the bis(dialkylmetal) oxalates, which have been studied extensively

[2, 4], by formal exchange of two oxygen atoms against two N—CH_3 functions. Therefore, we were interested to see whether the structural principle of the oxalates, which has been confirmed by X-ray analysis, also holds for the oxamide compounds, and whether, by aid of vibration and of ^1H and ^{13}C NMR spectroscopy, the presence of two configurational isomers could be established, as for the closely related dialkylmetal derivatives of *N*-methylacetamide [5].

2. Preparation and properties

Following the procedure for the bis(dialkylmetal) oxalates of gallium and indium [2], we treated the trialkyl derivatives of these elements, dissolved in ether or in benzene, with *N*,*N'*-dimethyloxamide [6] (NMOxA) in 2/1 molar ratio. NMOxA was added to the trialkyl solution batchwise, either in solid form or suspended in ether or benzene. Usually, a slight excess of trialkylmetal was used to suppress secondary reactions. Except with anhydrous oxalic acid, bis(dialkylaluminium) compounds could also be isolated in the oxamide series. Some characteristic physical properties are listed in Table 1.

The solubility of the bis(dimethylmetal) oxamides in organic solvents of low or medium polarity (CCl_4, C_6H_6, $CHCl_3$, CH_2Cl_2) is about the same for the aluminium and gallium products, but for the indium derivative, it is very much lower. The ethyl homologues of the two lighter elements are liquids at room temperature, and completely miscible with the solvents mentioned; the indium compound, again, is only slightly soluble. Solubility permitting, the oxamides could be shown cryoscopically to exist in the monomeric form in benzene. The sublimation residues, however, of which there is an appreciable amount, especially in the case of V and VI, are mainly polymeric bis(dialkylmetal) oxamides, according to elemental analysis and vibration spectra. Since they could not be purified satisfactorily, they were not studied in greater detail.

The sensitivity of the monomeric compounds towards atmospheric oxygen is in agreement with results reported so far for organometallic derivatives of Group III elements, i.e., a decrease in decomposition tendency from the aluminium to the indium derivative. The behaviour towards water, however, is unusual. As a rule, sensitivity towards hydrolysis is lowered as the reactivity of the metal—carbon bond goes down from the aluminium to the indium compounds, paralleled by an increase in ionic character. Hydrolysis affords, besides alkane

TABLE 1

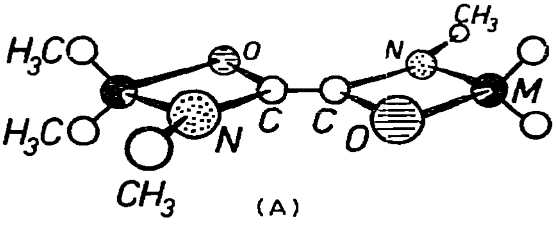
PHYSICAL DATA OF BIS(DIALKYLMETAL)-*N*,*N'*-DIMETHYLOXAMIDES

Number	Compound	M.p. (°C)	B.p. (°C/mm Hg)	Subl. p. (°C/mm Hg)
I	$[(CH_3)_2Al]_2[C_2O_2(NCH_3)_2]$	118	—	$70/10^{-2}$
II	$[(C_2H_5)_2Al]_2[C_2O_2(NCH_3)_2]$		$90/10^{-4}$	
IIIa	$[(CH_3)_2Ga]_2[C_2O_2(NCH_3)_2]$	90-92		80/0.5 or $35/10^{-4}$
IIIb	$[(CD_3)_2Ga]_2[C_2O_2(NCH_3)_2]$			
IV	$[(C_2H_5)_2Ga]_2[C_2O_2(NCH_3)_2]$	~7	$88/10^{-3}$	—
V	$[(CH_3)_2In]_2[C_2O_2(NCH_3)_2]$	160-163	—	$130/10^{-4}$
VI	$[(C_2H_5)_2In]_2[C_2O_2(NCH_3)_2]$	133-136	—	$90/10^{-4}$

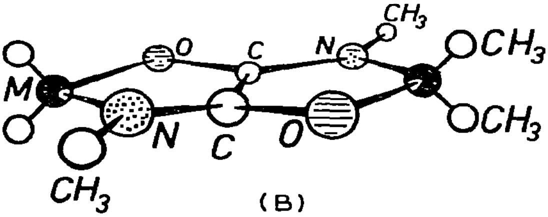
and metal hydrates or, less frequently, stable dialkylmetal cations, stable ligand anions such as Cl^-, CH_3COO^-, $O_2PF_2^-$, $CH_3SO_3^-$ etc. [7]. For the NMOxA derivatives, solubility behaviour in organic solvents indicates "regular" increase in ionic character from aluminium to indium. Besides the decreasing reactivity of the metal—carbon bond, however, the instability of the $C_2O_2(NCH_3)_2^{2-}$ anion has also to be taken into account. Upon hydrolysis, free NMOxA is formed immediately as evidenced by the the appearance of an intense N—H stretching bond in the IR spectra. Thus, H_2O attacks the aluminium derivatives by breaking up the Al—C bond; with the extremely sensitive indium homologues, the free *N,N'*-dimethyloxamide is formed in the first step. The gallium compounds, on the other hand, are remarkably stable towards water, suffering appreciable decomposition only above 40°C.

3. Mass spectral analysis

For the structure of the monomeric bis(dialkylmetal) derivatives of NMOxA, two models are to be considered: A and B. As in the case of the analogous oxalates [2], it is not possible to differentiate between these two basic structures by vibration spectroscopy. For the oxalate complexes, the fused five-membered ring structure has been established unequivocally by X-ray analysis [4]. If the NMOxA derivatives also exist in this form, there should be significant similarity in the mass spectra of both classes of compounds.



(A)



(B)

Elementary gallium is composed of two isotopes of mass 69 and 71, with a natural abundance of 60.4 to 39.6%, respectively. Therefore, in the mass spectrum all fragments containing one gallium atom give rise to a doublet with a spacing of two mass units and relative intensity 100/65.6. Fragments incorporating two gallium atoms appear as triplets; again, the three lines are separated from each other by two mass units, and their intensity ratio should be 76.3/100/32.8.

In the mass spectrum of the bis(dimethylgallium)-*N,N'*-dimethyloxamide (IIIa), the molecular ion peak is missing (*m/e* 312, 314, 316); at *M* — 1, a very weak triplet is just discernible (Table 2). The base peak of the spectrum is

TABLE 2

MASS SPECTRAL DATA OF BIS(DIMETHYLGALLIUM)-*N,N'*-DIMETHYLOXAMIDE (IIIa) AND BIS(HEXADEUTERODIMETHYLGALLIUM)-*N,N'*-DIMETHYLOXAMIDE (IIIb)[a]

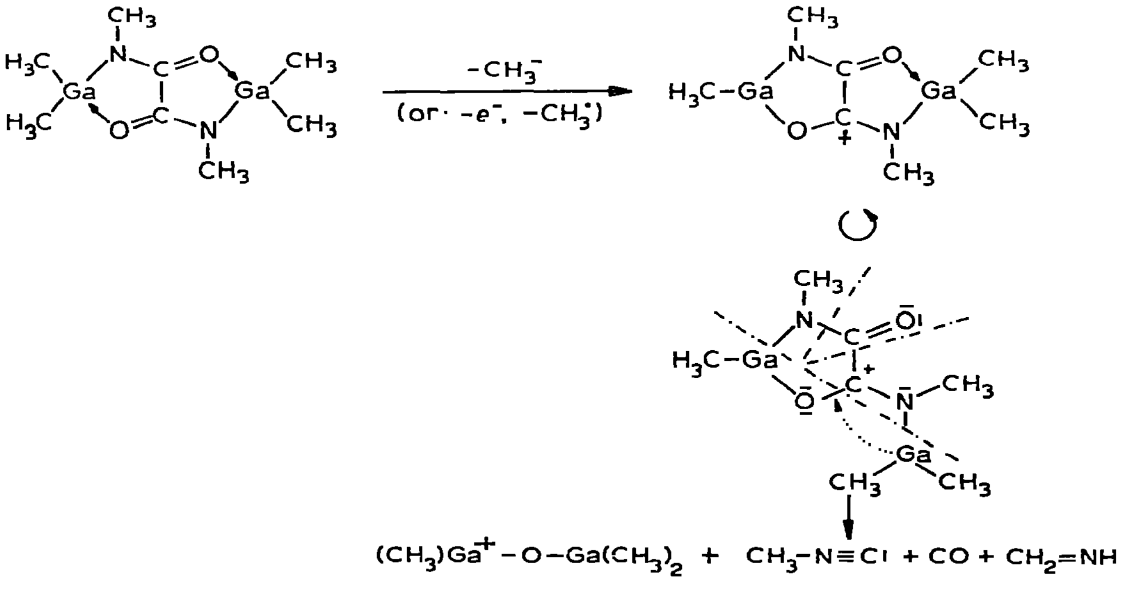
IIIa (M^+ 312, 314, 316)				IIIb (M^+ 324, 326, 328)		
I/base[b] (%)	*m/e*	Fragmentation	Fragment ion	Fragmentation	*m/e*	*I*/base[b] (%)
	311, 313, 315[c]	$M - H$				
7.6	298, 300, 302	$(P + 1)$				
(100.0) 100.0	297, 299, 301 (76.5, 100, 35.0%)	$M - (CH_3)$[d]	$(CH_3)_2Ga[(CH_3N)OCCO(NCH_3)]Ga(CH_3)^+$	$M - (CD_3)$	306, 308, 310 (76.0, 100, 34.7%)	100.0 (100.0)
(0.8) 14.4	141, 142, 143 ≙282, 284, 286	$M - 2(CH_3)$	$(CH_3)Ga[(CH_3N)OCCO(NCH_3)]Ga(CH_3)^{2+}$	$M - 2(CD_3)$	144, 145, 146 ≙288, 290, 292	13.4 (0.9)
1.2	281, 283, 285	$M - 2(CH_3)H$	$(CH_3)Ga[(CH_2{=}N)OCCO(NCH_3)]Ga(CH_3)^+$	$M - 2(CD_3)H$	287, 289, 291	0.5
(2.8) 7.3	267, 269, 271	$M - 3(CH_3)\cdot$	$(CH_3)Ga[(CH_3N)OCCO(NCH_3)]Ga^+$	$M - 3(CD_3)$	270, 272, 274	5.9 (3.1)
(3.8) 5.4	240, 242, 244	$M - (CH_3)$ $(CONCH_3)$	$(CH_3)_2Ga(CONCH_3)Ga(CH_3)^+$		249, 251, 253	3.6 (2.2)
1.6	210, 212, 214	$M - 3(CH_3)$- $(CONCH_3)$	$(CH_3)Ga(CONCH_3)Ga^+$		213, 215, 217	0.9
(10.4) 22.4	199, 201, 203	[d]	$(CH_3)_2GaOGa(CH_3)^+$		208, 210, 212	19.8 (9.0)
1.8	183, 185, 187		$(CH_3)_2GaGa(CH_3)^+$		192, 194, 196	1.2
(1.1) 8.6	169, 171, 173		$(CH_3)Ga_2O^+$		172, 174, 176	7.7 (0.9)
1.0	153, 155, 157		$(CH_3)Ga_2^+$		156, 158, 160	0.9
1.8	126, 128		$Ga(CONCH_3)^+$		126, 128	1.7
1.0.	112, 114		?			
(2.7) 16.6	99, 101		$(CH_3)_2Ga^+$		105, 107	19.4 (3.4)
1.1	84, 86		$(CH_3)Ga^+$		87, 89	1.5
(0.7) 9.5	69, 71		Ga^+		69, 71	9.6 (0.8)
	28		CO^+		28	

[a] The mass spectra as reported here have been run on a Varian MAT 711 equipped with a Varian 620i computer: ionization energy 70 eV, source current 0.8 mA, source temperature 196°C, inlet temperature —7°C resolution 800. [b] The values in brackets give the relative intensities of 25 eV spectra (run under the same probe conditions). [c] This triplet could be recognized only in a mass spectrum recorded by a five element galvanometer trace. [d] In the most sensitive galvanometer trace, two metastable peaks appear at *m/e* 133.3 and 136.9, corresponding to a decomposition 297 → 199 ($199^2/297 = 133.3$), and 301 → 203 ($203^2/301 = 136.6$) (the inner signal is obscured by a sharp line).

represented by the middle line of a triplet at *m/e* 297, 299, 301 (*M* — 15); with 76.5/100/35.0, the intensity distribution is within experimental error equal to the theoretical one. The three signals are each accompanied by a (*P* + 1) isotope peak of 7.6% main line intensity, almost exactly the value required for 7 C. The fragment ion responsible for these peaks is formed by cleavage of CH_3 from a gallium atom as shown by comparison with the mass spectrum of compound IIIb which bears two CD_3 groups at each gallium atom (Table 2, right hand column). Here, a triplet at 306, 308, 310 provides the base peak, shifted to higher mass numbers by 9 units; due to incomplete deuteration, there are more satellite signals with an intensity pattern somewhat different from that found for IIIa. The fragment corresponding to a loss of two metal-bound CH_3 groups appears as a double-charged species at *m/e* 141, 142, 143, equivalent to mass numbers 282, 284, 286; the assignment is confirmed by correlation with the analogous triplet in the spectrum of the deuterated compound (*m/e* 144, 145, 146 ≙ 288, 290, 292 mass units). Since there is no trace of the singly-charged species in either mass spectrum, it is not unreasonable to suppose that, upon electron impact, one or two methyls are expelled as anions. The fragment sequence of both IIIa and IIIb then continues with a rather intense triplet retaining one metal-bound CH_3 group, and with two fragments, which, besides lacking respectively one and three methyls, have lost half the oxamide skeleton.

The fragment appearing at *m/e* 199, 201, 203 correlates with the 208, 210, 212 triplet of the deuterated compound, and thus must retain both gallium atoms and three of the four metallic-bound methyl groups. This means that the oxamide function has been completely eliminated except for one oxygen in producing the 199, 201, 203 moiety. Furthermore, metastable peaks at 133.3 and 136.9 give unequivocal proof that the fragment is formed directly from the ion with *m/e* 297, 299, 301 (see footnote *d*, Table 2). This fragmentation, which at first seems rather obscure, may be rationalized in terms of Scheme 1.

SCHEME 1



In the first step, a methyl group is cleaved, either as $CH_3^{\cdot}$ from the radical cation or directly from the neutral molecule as CH_3^-, from one gallium atom which compensates for its loss of electrons by forming a covalent bond to the neighbouring carbonyl oxygen. After breaking the (loose) coordinative bond at the other gallium, the $Ga(CH_3)_2$ function can be transferred to the oxidic oxygen; successive cleavage of three stable neutral molecules, CO, CH_3NC and $CH_2{=}NH$, leaves the fragment $(CH_3)_3Ga_2O^+$. The ion which has completely eliminated the central *N*,*N'*-dimethyloxamide moiety appears at *m/e* 183, 185, 187 with ten-fold less intensity. Further elimination of ethane from these two species affords $CH_3Ga_2O^+$ and $CH_3Ga_2^{\dot{+}}$ (8.6 and 1.0% intensity respectively of the basis triplet). Then, there are strong signals for $(CH_3)_2Ga^+$ and for gallium ions completely stripped while CH_3Ga^+ can only just be recognized. A doublet at 126, 128 provides the only coincidence between the spectra of IIIa and IIIb; this fragment, therefore, no longer contains any metal-bound CH_3 or CD_3 group, respectively, and thence must be assigned the structure $Ga(CONCH_3)^+$.

By means of the characteristic gallium isotope pattern, and by correlation of CH_3 with CD_3 compound, all significant peaks in the mass spectrum of IIIa could be assigned unequivocally. It is instructive now to compare the spectra of bis(dimethyl)-*N*,*N'*-dimethyloxamide (IIIa) and bis(dimethylgallium)oxalate (VII) (Table 3). In the spectrum of VII run with 70 eV ionization energy, the

TABLE 3

MASS SPECTRAL DATA OF BIS(DIMETHYLGALLIUM)OXALATE (VII) AND BIS(DIMETHYLGALLIUM)-*N*,*N'*-DIMETHYLOXAMIDE (IIIa)[a]

VII (M^+ 286, 288, 290)

I/base (%)	*m/e*	Fragmentation	Fragment ion
5.3	272, 274, 276	*P* + 1	
100.0[b]	271, 273, 275	*M* − (CH_3)	$(CH_3)_2Ga(O_2C{-}CO_2)Ga(CH_3)^+$
	(76.7, 100, 33.0%)		
7.7	128, 129, 130[c]	*M* − $2(CH_3)$	$(CH_3)Ga(O_2C{-}CO_2)Ga(CH_3)^{2+}$
	≙ 256, 258, 260		
	(76.5, 100, 37.0%)		
	—		—
4.5	242, 244, 246	*M* − (CO_2)	$(CH_3)_2Ga(CO_2)GA(CH_3)_2^{\dot{+}}$
3.8	241, 243, 245[c]	*M* − $3(CH_3)$	$(CH_3)Ga(O_2C{-}CO_2)Ga^+$
	—		—
	—		—
56.3	199, 201, 203		$(CH_3)_2GaOGa(CH_3)^+$
19.2	198, 200, 202	*M* − $2(CO_2)$	$(CH_3)_2GaGa(CH_3)_2^{\dot{+}}$
14.9	183, 185, 187		$(CH_3)_2GaGa(CH_3)^+$
12.3	169, 171, 173		$(CH_3)Ga_2O^+$
2.1	153, 155, 157[c]		$(CH_3)Ga_2^+$
	—		—
67.8	99, 101		$(CH_3)_2Ga^+$
7.3	84, 86		$(CH_3)Ga^+$
38.9	69, 71		Ga^+

[a] For technical details of the mass spectra see Table 2, note *a*. [b] Base peak of the 70 eV spectrum is the CO/N_2 signal at *m/e* 28. The relative intensities have been recalculated using the 273-peak as 100% standard. [c] Peaks not detectable in a 25 eV spectrum.

CO^+ signal (*m/e* 28) is the base peak; on reduction of the ionization energy to 25 eV, however, the intensity base is shifted to the strongest line of the (M — 15) fragment. 70 eV traces of both IIIa and VII are compared in Table 3; for VII, the intensities have been re-evaluated, referring to the middle peak of the 271, 273, 275 triplet as 100%. In the region above 200 mass units, the two spectra are congruent to a large degree with respect to fragmentation pattern and intensity distribution. Of course VII lacks the fragment (M — $2CH_3$—H) since the lone hydrogen stems from the *N*-methyl function, as well as the two ions produced by degradation of the oxamide backbone. Because of the easy cleavage of carbon dioxide as a neutral molecule, on the other hand, there are two additional triplets in the oxalate spectrum corresponding to the loss of one (242, 244, 246) and two moles CO_2 (198, 200, 202, intense signal) from the molecular ion. The fragment $(CH_3)_2Ga_2O^+$ (*m/e* 199, 201, 203), however, is far more intense, even for VII. Since the elimination of CO_2 and CO responsible for this peak is a more facile process than the analogous cleavage of CO, CH_3NC, and CH_2NH for the oxamide, the fragment 199, 201, 203 is much more pronounced in the spectrum of VII than in that of IIIa. At lower mass numbers, all fragments are present in both spectra except for $Ga(CONCH_3)^+$; due to the fragmentation line $M^+ - 2CO_2 \rightarrow (CH_3)_2Ga_2(CH_3)_2^+ \rightarrow ...$, however, the ions $(CH_3)_2Ga^+$, CH_3Ga^+, and Ga^+ appear with higher intensity for VII than they do in the case of IIIa (Table 3).

IIIa (M^+ 312, 314, 316)

Fragment ion	Fragmentation	*m/e*	*I*/base (%)
	$P + 1$	298, 300, 302	7.6
$(CH_3)_2Ga[(CH_3N)OC{-}CO(NCH_3)]Ga(CH_3)^+$	$M - (CH_3)$	297, 299, 301 (76.5, 100, 35.0%)	100.0
$(CH_3)Ga[(CH_3N)OC{-}CO(NCH_3)]Ga(CH_3)^{2+}$	$M - 2(CH_3)$	141, 142, 143 ≘ 282, 284, 286	14.4
$(CH_3)Ga[(CH_2{=}N)OC{-}CO(NCH_3)]Ga(CH_3)^+$	$M - 2(CH_3)H$	281, 283, 285	1.2
—		—	
$(CH_3)Ga[(CH_3N)OC{-}CO(NCH_3)]Ga^+$	$M - 3(CH_3)$	267, 269, 271	7.3
$(CH_3)_2Ga[CO(NCH_3)]Ga(CH_3)^+$	$M - (CH_3)(CONCH_3)$	240, 242, 244	5.4
$(CH_3)Ga[CO(NCH_3)]Ga^+$	$M - 3(CH_3)(CONCH_3)$	210, 212, 214	1.6
$(CH_3)_2GaOGa(CH_3)^+$		199, 201, 203	22.4
—		—	
$(CH_3)_2GaGa(CH_3)^+$		183, 185, 187	1.8
$(CH_3)Ga_2O^+$		169, 171, 173	8.6
$(CH_3)Ga_2{}^+$		153, 155, 157	1.0
$Ga(CONCH_3)^+$		126, 128	1.8
$(CH_3)_2Ga^+$		99, 101	16.6
$(CH_3)Ga^+$		84, 86	1.1
Ga^+		69, 71	9.5

For bis(dimethylgallium)oxalate, the fused five-membered ring structure is established by X-ray analysis. The virtually identical fragmentation behaviour of the oxalate VII and the oxamide IIIa, especially in the formation of the ion $(CH_3)_3Ga_2O^+$, hence provides sufficient proof that bis(dimethylgallium)-*N,N'*-dimethyloxamide exists in the same configuration. In the following paragraphs, this conclusion will be confirmed by means of ^{1}H and ^{13}C NMR and of IR and Raman spectra, mainly for the homologues I, II, IV, V and VI not subjected to mass spectral analysis. Furthermore, these spectroscopic methods should provide a deeper insight into the fine structure of the oxamide complexes.

4. ^{13}C and ^{1}H NMR data

^{13}C chemical shift parameters (in $CDCl_3$ solution) and C—H coupling constants of the bis(dialkylmetal)-*N,N'*-dimethyloxamides (I-IV) are listed in Table 4; for the indium homologues V and VI, decomposition is too fast in deuterochloroform to allow ^{13}C measurements to be made. In each case, the oxamides were dissolved in $CDCl_3$ to the saturation limit; spectra were run first with proton noise decoupling, secondly with gated decoupling. Only then, TMS was added, and fully decoupled spectra were recorded again. In the case of the aluminium compounds, the resonances of the carbon atoms bound directly to the metal appear shifted to higher field by 0.5 ppm relative to the $CDCl_3$ signal, those of the β-C atoms by 0.1 ppm even though the amount of TMS used was less than 5% of the solute. For the resonances of carbonyl and N-methyl carbons, on the other hand, divergence between spectra with and without TMS was well within the limit of experimental error. The gallium oxamides, also, did not show this discrepancy. Therefore, all resonances were measured as relative to $CDCl_3$ in solutions without TMS, and then converted to the $\delta_{(TMS)}$ scale with $\delta_{(CDCl_3)}$ 76.91 ppm [8].

For the aluminium compounds I and II, the carbonyl ^{13}C resonances are right within the range given for carboxylic acid derivatives [9] (e.g. $HCON(CH_3)_2$ δ 164.9 ppm). In a structure with two fused five-membered rings, the N-methyl group is inevitably *cis* to the carbonyl function and should thus experience an upfield shift because of the electric field gradient of the C=O bond [10] but, since ^{13}C data on N-substituted oxamides are not available, comment on the N-CH_3 shift is not possible. By one- and three-bond coupling with the N-methyl protons, N-CH_3 and carbonyl resonances are each split into well resolved quadruplets in the undecoupled spectra, ^1J as well as ^3J being identical for I and II. For the metal-bound alkyl groups, α-carbon shifts are at high field relative to TMS; both CH_3 and CH_2 lines are severely broadened ($\nu_{1/2}$ 60 resp. 40 Hz) due to the neighbouring quadrupolar aluminium nucleus. With $\Delta\delta$ + 9.87 ppm, the metal-bound carbon experiences the expected α-shift in going from methyl to ethyl derivatives [11]. A small downfield shift of ~0.5 ppm is also observed for $\delta_{(CO)}$ and $\delta_{(NCH_3)}$.

By comparison of the chemical shifts for the ethyl derivatives of aluminium and gallium, II and IV, one notes constancy of $\delta_{(CO)}$ and a 0.7 ppm downfield shift for N-CH_3. The carbon α to the metal, however, appears less shielded by 5.1 ppm; this "paramagnetic" effect extends also to the β-methyl group, $\Delta\delta$ + 0.9 ppm. Electronegativity decreases down a group in the periodic table; the

TABLE 4

^{13}C NMR DATA OF BIS(DIALKYLMETAL)-*N*,*N*′-DIMETHYLOXAMIDES (I-IV) AND BIS(DIMETHYLGALLIUM)OXALATE (VII)
(saturated solution in $CDCl_3$, δ(ppm) relative to TMS, J(Hz))[a]

Compound	Metal M	CO		N—CH_3		R	MR		
		$\delta^b(\nu_{1/2})^c$	$^3J_{(CNCH_3)}{}^d$	$\delta(\nu_{1/2})$	$^1J_{(CH)}$		$\delta(\nu_{1/2})$	$^1J_{(CH)}$	$^2J_{(CCH)}$
I	Al	163.99 (5.0)	5.5	28.88 (6.0)	139.5	CH_3	CH_3 −12.16 (60)	113.5	
II	Al	164.50 (3.5)	4.5	29.26 (3.5)	139.5	C_2H_5	CH_3 8.04 (4.5) CH_2 −2.3 (40)	124.5 ~110	4.5 ?
IIIa	*Ga*	163.71 (3.0)	4.5	29.79 (3.0)	138.0	CH_3	CH_3' −7.54 (7.5)	122.5	
		163.11 (3.0)	5.0	29.29 (3.0)	138.0		CH_3(A) −6.22 (7.5) CH_3(B) −9.42 (8.5)	123.0 122.0	
IIIb	Ga	163.73 (2.0)		29.77 (3.5)		CD_3	CD_3' −8.44	19.0[c]	
		163.14 (2.0)		29.26 (2.0)			CD_3(A) −7.09 CD_3(B) −10.34	18.8 19.3	
IV	Ga	164.49 (1.5)	5.5	29.97 (1.5)	138.0	C_2H_5	CH_3 8.95 (1.5) CH_2 2.85 (3.5)	125.5 123.0	5.8 5.8
VII[f]	Ga	167.01 (2.0)		= —O—		CH_3	CH_3 −5.77 (7.5)		

[a] All spectra were taken of nearly saturated solutions of the oxamides in $CDCl_3$, at 30°C. The spectrometer system consisted of a Bruker HX 90 E with 15″ magnet, B-SV 3 PM pulse unit equipped with B-GD 1 multipulser, Nicolet BNC 12 computer (12 *k*), and a B-SV 3 B broad band decoupler. Pulse width for noise decoupled spectra was 2 μsec, decoupling power usually 20 watts, and dwell time/address 84 μsec corresponding to a sweep width of 5952.381 Hz. For the gated experiments, pulse width was increased to 3 μsec; the repetition time between successive pulse sequences was 3.0 sec, with an acquisition time of 0.344 sec for 4 *k*, 0.688 sec for 8 *k* interferograms. Depending on signal intensity, FIDs were stored into 4 *k* or 8 *k* computer space, respectively. To avoid undesirable line broadening, exponential multiplication was limited to TC = −1.5 for 4*k* and to TC = −3 for 8 *k* interferograms. 8 *k* computer space was used regularly for Fourier transformation, giving a resolution of 1.4532 Hz or 0.064 ppm per address. [b] Within a given spectrum, chemical shift differences are believed to be exact to within ± 0.02 ppm; absolutely, the error limit is ± 0.04 ppm. [c] The numbers in brackets give the half-height line widths, $\nu_{1/2}$, in Hz. [d] The coupling constants were taken from fully ^{13}C—^1H coupled spectra obtained by gated decoupling technique. Since they represent average values for multiplet spacing, they should be correct to ± 0.5 Hz. [e] $^1J_{(CD)}$ values were taken from a ^1H noise decoupled spectrum. [f] Since the oxalate is almost insoluble in $CDCl_3$, 500 000 pulses were required to obtain a S/N of 4/1 for the carbonyl C, and a gated decoupling spectrum was not taken.

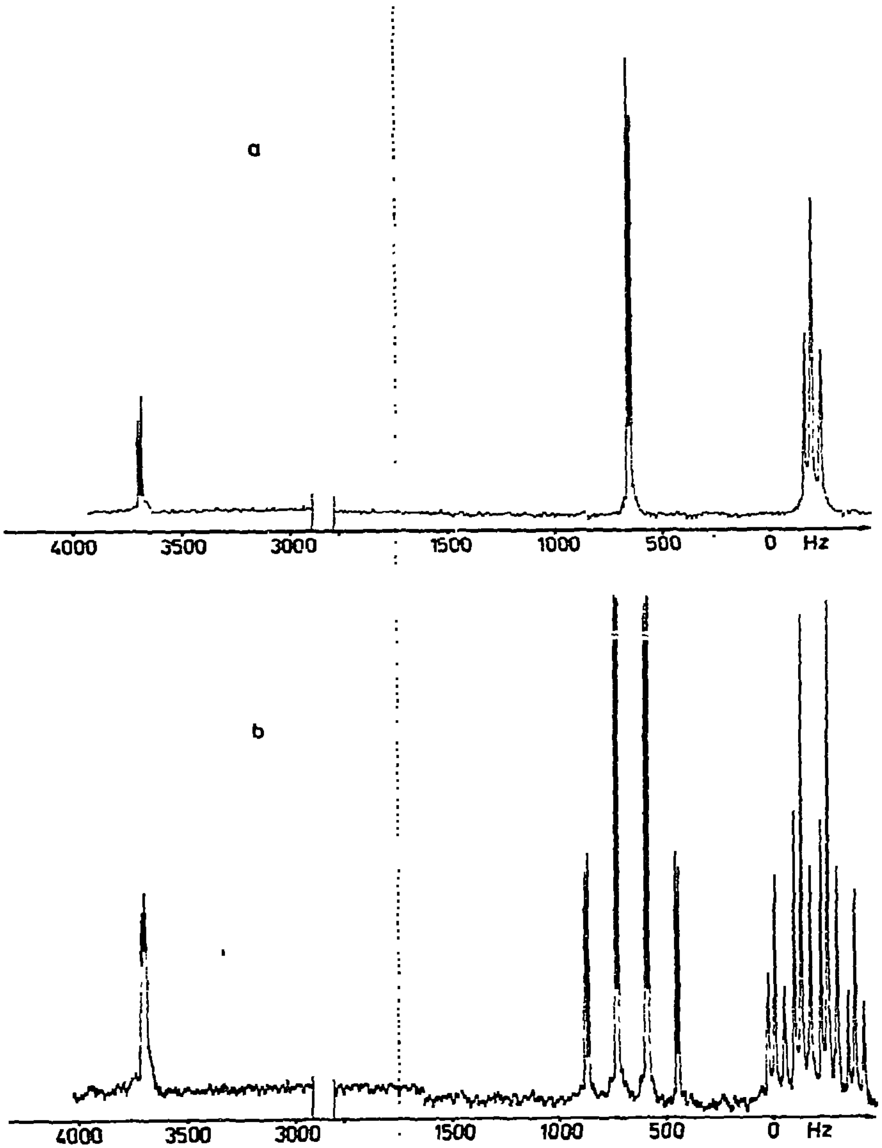
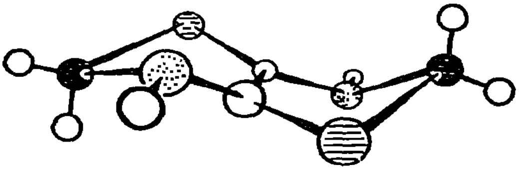
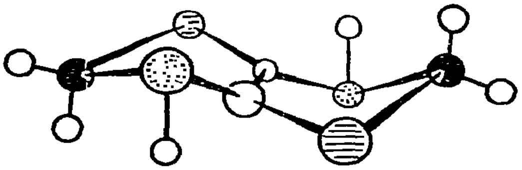


Fig. 1. ^{13}C NMR spectrum of bis(dimethylgallium)-*N*,*N'*-dimethyloxamide (IIIa), in CDCl$_3$ (the dashed line represents the middle signal of the CDCl$_3$ triplet): (a) with proton noise-decoupling, (b) undecoupled (gated decoupling technique).

concomitant increase in electron density at the α-C should thus result in better shielding of gallium relative to aluminium-bound carbon. Since transition energies (ΔE), on the other hand, decrease down a group, the σ_p contribution to the total shielding is expected to be enhanced. The consequent downfield shift may well override the effect of bond polarization, especially as the electronegativity difference between aluminium and gallium is very small indeed.

Despite this surprising downfield shift, interpretation of the oxamide ^{13}C spectra so far has been straightforward and well in accordance with the proposed planar structure B. In the spectrum of the dimethylgallium derivative IIIa, however, two lines appear of equal intensity for both carbonyl and N-methyl carbons (Fig. 1a). The Ga-CH_3 resonance is split into three lines with 1/2/1 relative intensity. One set of CO and NCH_3 resonances and the central Ga-CH_3 line might be attributed to the planar structure B. Of the two smaller lines of the "triplet", one is shifted to higher, one to lower field, with the mean frequency 0.28 ppm upfield from the middle line. This nonequivalence of the metal-bound methyl groups is possible only in a non-planar, twisted structure in which the two CH_3 groups have different orientation relative to the oxamide skeleton. Since both groups of lines are of equal intensity, the two conformers which are present for IIIa must have about the same energy. If the structure with two absolutely planar fused five-membered rings, for which maximum overlap between nitrogen lone pair and carbonyl π-bond occurs, is sterically feasible, it is not reasonable to suppose that a twisted conformation should have practically identical energy, and that this phenomenon should be limited exclusively to the $Ga(CH_3)_2$ case, for in the spectrum of IV not the least indication of any splitting is detectable, as shown in Fig. 2a. Rather, two "quasi-chair" conformations may be envisaged, C and D, differing only in the relative orientation of N-CH_3 and Ga-CH_3 groups.


(C)


(D)

In C, the N-CH_3 group is in a staggered position relative to the two gallium-methyl groups while in D it is eclipsed to one metal-bound CH_3 group and does not interact with the other one. Crowding of two methyl substituents in a cyclic structure generally results in an upfield shift; thus, the line at −9.42 ppm is assigned to the gallium-methyl *cis* to N-CH_3. In C, the N—C bond bisects the H_3C—Ga—CH_3 angle giving intermediate steric interaction for both metal-bound alkyl groups. Consequently, $\delta_{(GaCH_3)}$ in C is about halfway in between the values for "axial" and "equatorial" CH_3-in D. The assignment of the high field CO and N-CH_3 resonances relies upon the same argument but is by no means conclusive. None the less, by assuming an equilibrium mixture of C and D for IIIa, all ^{13}C resonance lines can be structurally rationalized.

^{13}C—^{1}H coupling of the metal-bound alkyl substituents provide a further structural parameter still to be discussed. In I, the $^{1}J_{(CH)}$ values of 113.5 Hz for the aluminium-bound methyl groups is practically identical with the coupling constant reported for dimeric $Al(CH_3)_3$ [12]. For II, $^{1}J_{(C-\alpha, H)}$ is about 110 Hz, a more precise determination being impossible since the CH_2 lines are extremely broad, further split by $^{2}J_{(CCH)}$, and, in the undecoupled spectra, superimposed by CH_3 resonances. With IIIa and IV, the resonance lines of the metal-bound carbons are much less broadened than in the case of the aluminium compounds, indicating faster quadrupolar relaxation for the gallium derivatives. Thus, $^{1}J_{(CH)}$ and $^{2}J_{(CCH)}$ of both C_α and C_β could be determined with high precision for the $Ga(C_2H_5)_2$ product (Fig. 2b). The $^{1}J_{(C-\alpha, H)}$ value of 123.0 Hz again is nearly

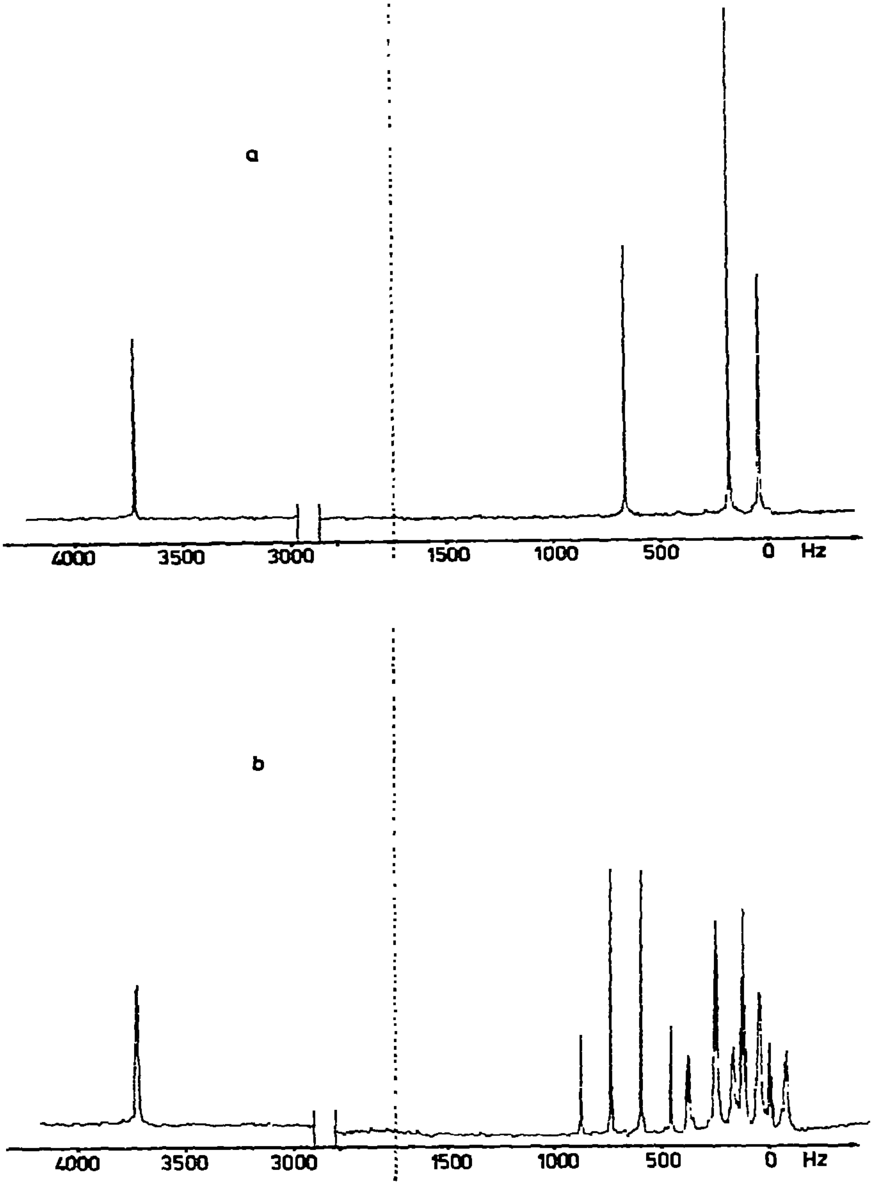


Fig. 2. ^{13}C NMR spectrum of bis(diethylgallium)-*N,N'*-dimethyloxamide (IV), in $CDCl_3$ (the dashed line represents the middle signal of the $CDCl_3$ triplet): (a) with proton noise-decoupling, (b) undecoupled (gated decoupling technique).

the same as for (monomeric) trimethylgallium [12] while $^1J_{(C-\beta,\ H)}$ shows regular alkane behaviour (125.5 Hz). For all three Ga-CH_3 quadruplets which appear in the undecoupled spectrum of IIIa, $^1J_{(CH)}$ is identical within the error limit, 122.5 ± 0.5 Hz (Fig. 1b).

As Dreeskamp and Sackmann [13] have shown, $^1J_{(XC-H)}$ is proportional to the product of the electronegativity of X and C—X bond length, and responds very sensitively to small changes in $r_{(C-X)}$. The identical values of $^1J_{(C-\alpha,\ H)}$ for

$Al(CH_3)_3$ and its oxamide derivatives, as well as for $Ga(CH_3)_3$ and its derivatives IIIa and IV, thus clearly indicate that the metal—carbon bonds in I to IV are virtually unchanged from the parent compounds, and that the isomerism giving rise to the nonequivalent $GaCH_3$ groups in IIIa must be due to a conformational process rather than a change in basic structure. To test this conclusion, we shall now examine the ^{13}C spectrum of the hexadeuterodimethylgallium oxamide IIIb.

Within the error limit of the Fourier spectrum, the chemical shifts of both CO and N-CH_3 carbons are identical for IIIa and IIIb. The Ga—C resonance should be split into a heptuplet by coupling with three deuterium nuclei; as in the case of IIIa, however, there are three groups of signals with seven lines each, the central one again of two-fold intensity. $^1J_{(CD)}$ coupling evaluated as average spacing of all the lines of a multiplet varies somewhat for the three groups; since divergence is well within the error limit, though, the 19.0 Hz for the more intense heptuplet should be accepted as mean value. This corresponds well with the $^1J_{(CH)}$ coupling constant of IIIa ($19.0 \times 6.51 = 123.7$ vs. 122.5 Hz). All three CD_3 carbon atoms are better shielded by 0.90 ± 0.03 ppm relative to the CH_3 homologue, the isotope shift being in good agreement with literature data [8].

The slight difference in electron affinity and steric requirements of CD_3 as compared with CH_3 substituents thus does not affect the conformational equilibrium of gallium *N*,*N'*-dimethyloxamide. Changing the metal-bound alkyl group from methyl to ethyl, however, does already suffice to suppress the "asymmetric conformer" D. Since the N—Al bond is much shorter than the N—Ga bond, interaction between metal-bound alkyl and N-methyl groups is sufficiently large even for the $Al(CH_3)_2$ compound that only the staggered conformation C can be detected. From proton spectra (see below), the presence of both conformers in 1/1 ratio is again established for the $In(CH_3)_2$ oxamide. Further investigations in the gallium series will have to show whether it is possible by altering the N-alkyl substituent to influence the conformational equilibrium without shifting it completely in favour of C.

The ^1H NMR data of compounds I-V and VII are listed in Table 5. For the two ethyl derivatives of aluminium and gallium, methyl and methylene protons

TABLE 5

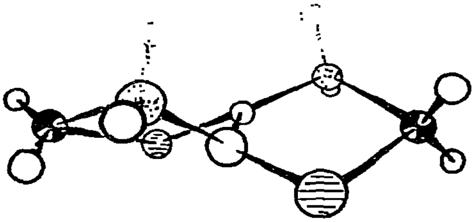
^1H NMR DATA OF BIS(DIALKYLMETAL)-*N*,*N'*-DIMETHYLOXAMIDES I-V AND BIS(DIMETHYLGALLIUM)OXALATE VII (saturated solution in $CDCl_3$, 30°, δ (ppm) relative to TMS)

Compound	metal M	N—CH_3	R	M—R		
				δ_α	δ_β	J(Hz)
I	Al	2.90	CH_3	CH_3 -0.68		
II	Al	2.90	C_2H_5	CH_2 0.82	CH_3 -0.18	8.30
IIIa	Ga	2.90	CH_3	CH_3' -0.32		
				$CH_3(A)$ -0.24		
				$CH_3(B)$ -0.41		
IV	Ga	2.90	C_2H_5	CH_2 0.90	CH_3 0.36	8.20
V	In	2.90	CH_3	CH_3' -0.10		
				$CH_3(A)$ -0.02		
				$CH_3(B)$ -0.21		
VII	Ga	= —O—	CH_3	CH_3 0.02		

are rather closely coupled giving rise to spectra which deviate substantially from first order. By iterative computer analysis, however, all lines in the experimental spectrum could be reproduced satisfactorily with respect to both frequency and relative intensity. Thus, by establishing only one set of nuclei (A_3B_2) for the proton spectra also, the presence of but one conformer is confirmed for II and IV. As with ^{13}C, the α-protons are shifted to lower field in going from aluminium to gallium derivatives. The $Al(CH_3)_2$ derivative shows just one resonance each of $N\text{-}CH_3$ and metal-bound CH_3 groups. For the gallium homologue IIIa, the 60 MHz spectrum presents a single N-methyl line while the $Ga\text{-}CH_3$ part looks like a 1/2/1 triplet for which only very precise measurements show a slight asymmetry. The 50% increase of both spacings in a 90 MHz spectrum are proof, however, that the splitting is due to chemical nonequivalence and not to any coupling process. This "quasi-triplet" also characterizes the ^1H NMR spectrum of the $In(CH_3)_2$ derivative; the two outer lines are wider spaced, though, and not so symmetrical about the central one as for IIIa. Again, only one $N\text{-}CH_3$ resonance appears in the proton spectrum for both conformers, C and D.

5. Vibrational spectra

Apart from the frequency shifts expected for going from aluminium to indium products, IR and Raman spectra of compounds I-VI are of such similarity that for the whole series one basic structural principle must be assumed. Because of the splitting of the methyl resonances in the ^1H NMR spectrum, and of $M\text{-}CH_3$, $N\text{-}CH_3$, and CO signals in the ^{13}C NMR spectrum, IIIa, IIIb and V cannot have the planar structure B which has been established by both vibrational spectroscopy and X-ray analysis for mono- and bis(tetrachloroantimony)-*N,N'*-dimethyloxamide [14, 15]. Since vibrational evidence demands the same conformation for all derivatives, I-VI, B may therefore be excluded from further consideration. Besides the quasi-chair conformations C and D (point group S_2) which are reasonable structural models, however, another non-planar structure of C_2 symmetry, E, must be taken into account which is also in accord with ^1H and ^{13}C NMR data.



(E)

Structures C and D, with a planar $C_2O_2N_2$ backbone, possess a centre of symmetry while in E the OCN moieties of the central unit are more or less twisted relative to each other. Thus, models C, D and E may be differentiated by vibrational spectroscopy since, for the centrosymmetric structure, theory demands strict adherence to the alternating rules for many of the possible vibrations; for the "twisted" form E, the alternating rules do not hold. (On the other hand, it would not have been possible to differentiate the two centrosymmetrical structures B and C/D by means of IR and Raman spectra.)

TABLE 6

FREQUENCY VALUES FOR OCN STRETCHING BANDS OF NMOxA DERIVATIVES

		NMOxA [15, 16]	Al[a]	Ga[a]	In[a]	Li
ν_a(OCN) in-phase	only Raman	1690	1668	1651	1632	
ν_a(OCN) out-of-phase	only IR	1660	1652	1637	1603	1585
ν_s(OCN) in-phase	only Raman	1295	1449	1442	1413	
ν_s(OCN) out-of-phase	only IR	1238	1330	1333	1277	1272

[a] Average values of dimethyl and diethyl compounds.

Among the characteristic vibrations of the oxamide derivatives for which the theoretically required alternative behaviour should be especially pronounced, the OCN stretching vibrations are of first importance. There are two OCN functions which are strongly coupled across the central C—C bond, and thus give rise to both in-phase and out-of-phase stretching vibrations. For a centrosymmetrical structure, in-phase vibration bonds should appear only in the Raman, those due to out-of-phase movements exclusively in the IR spectrum. For the alternative structure depicted as E, theory demands all four vibrations to be present at identical wavelengths in both IR and Raman spectra. In Table 6 frequency values for OCN stretching bands are listed for the NMOxA derivatives; for comparison, data for free NMOxA and for the "salt" prepared from $LiCH_3$ and NMOxA are included. At first sight, the observed alternation of IR and Raman bands seems to provide clear evidence for conformation C, D. A slight distortion of the $O_2C_2N_2$ backbone, however, cannot be excluded; for bis(dimethylgallium) oxalate, a twist of 5-6° has been established in the solid state. There is some indication for similar distortion in the Raman spectra of the gallium and indium products: besides the symmetrical in-phase vibrations, the corresponding out-of-phase bands can be observed at extremely high gain, though with minimum intensity. Likewise, the asymmetric in-phase stretching is just visible in high concentration IR spectra. This is not sufficient evidence, though, to discredit the centrosymmetrical conformation. A small skeletal distortion should rather be regarded as slight perturbation of the centrosymmetric structural principle recognizable in the region of OCN bond stretching frequencies, but not for the OCN bending or OMN stretching bands.

From the above compilation of OCN stretching frequencies the increasingly ionic nature of the products on going from aluminium to indium again becomes apparent free NMOxA and the unstable Li "salt" providing the limiting values. Similar shifts are found in the spectral region of OMN stretching vibrations ($\nu < 600$ cm^{-1}). Correct assignments, however, are rather difficult here since CMC valence stretching is expected in the same frequency range, besides NMC, OCN, CH_3NC, CMC, and CCM bending bands. Of these, only CMC stretching can be assigned with reasonable certainty by virtue of band intensity and constant band energy. For this reason and also because of accidental degeneracy, only (narrow) frequency ranges are given for all other vibrational processes in Tables 7 and 8. The vibrational spectra of IIIa, IIIb and V do not offer unequivocal proof of the presence of two conformational isomers, C and D. Below 600 cm^{-1}, we observe

(continued on p. 35)

TABLE 7

VIBRATIONAL SPECTRAL DATA OF BIS(DIMETHYLMETAL)-*N*,*N*′-DIMETHYLOXAMIDES (I, IIIa, IIIb and V) (ν(cm^{-1}), Intensity[a])

$[(CH_3)_2Al]_2NMOxA$ (I)[b]		$[(CH_3)_2Ga]_2NMOxA$ (IIIa)[b]		$[(CD_3)_2Ga]_2NMOxA$ (IIIb)[b]		$[(CH_3)_2In]_2NMOxA$ (V)		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
—	1668 s(p)	1653 vw(sh)	1653 s(p)	1660 vw(sh)	1654 s(p)	—	1635 s	ν_a(OCN) in-phase
1649 vs	—	1640 vs	—	1644 vs	—	1610 vs(br)	—	ν_a(OCN) out-of-phase
1455 s(br)	1451 (sh)(dp)	1440 (sh)	(1443)[d]	1455 m-w	1448 (sh)(dp)	1451 w-m	1452 w	$\delta_a(CH_3)$ (N-, M-bound)
		1438 m		1444 m-w		1440 (sh)		
—	1448 vs(p)	—	1443 vs(p)	—	1442 s(p)	—	1414 s	ν_s(OCN) in-phase
1405 m	1410 (sh)(dp)	1405 s-m	1411 vw(dp)	1411 s-m	1418 w(dp)	1402 s-m	(1414)	$\delta_s(CH_3\text{-}N)$ + overtone
1395 (sh)	1385 vw(p)	1395 (sh)	1390 vw(br)(p)	1395 (sh)	1395 (sh)	(1396)	1389 w-m	
		1382 w				1396 m		
1329 s	—	1330 s	1337 vvw	1338 s	1341 vvw	1275 s(br)	—	ν_s(OCN) out-of-phase
1189 m-s	1196 vs(p)	1202 m	1209 vs(p)	—	—	1170 w-m	1178 s-m	$\delta_s(CH_3\text{-}M)$
		1196 w-m				1156 w-m	1158 s-m	
(1189)		1182 (sh)		1188 w		(1170)	(1178)	ρ, $\gamma(CH_3)$ (N-, M-bound)
	1106 vw(p)	1095 w	1104 vw(p)	1103 w	1094 w(br)(p)	1105 w	1110 vw	
			1088 vw(p)	1097 w			1085 vw	
1026 vw		1028 w		1037 w-m				
1002 m	—	1006 w-m	—	1011 w-m	—	997 m	—	$\nu(N\text{-}CH_3)$ out-of-phase
					986 vw(br)			$\delta(CD_3—Ga)$ (?)
				947 m	941 vs(p)			$\delta_s(CD_3—Ga)$
—	934 m(p)	—	925 w(p)	935 (sh)	(941)	—	912 w	$\nu(N—CH_3)$ in-phase + ν(C—C)
849 s-m	—	835 m	—	839 m	—	819 m	—	δ(OCN) out-of-phase
—	813 w(dp)	—	813 w(dp)	—	814 w(dp)	—	810 w	δ(OCN) in-phase

720 (sh)	734 vw(br)	760 (sh)				720 s-m(br)		$\rho(CH_3—M)(+\nu_a(AlC_2))$	
694 s	697 m (dp)	731 s-m	675 vw(br)				680 vw(br)		
605 s-m	605 s(p)	—	—	—	—	—	—	$\nu(AlO)$	+ $\delta(OCN)$
—	—	603 (sh)	610 vw	595 (sh)	593 vvw	589 m	—		
—	—	(589)	595 w-m(dp)	(580)	—	—	—		
—	—	589 s-m	587 w-m(dp)	—	—	—	—	$\nu_a(GaC_2)$	
—	—	—	—	580 s	575 vw	—	—	$\rho(CD_3—Ga)$	
580 (sh)	581 vs(p)	—	—	—	—	—	—	$\nu_s(AlC_2)$	
572 w-m	—	572 m	—	(580)	—	—	565 w		
—	—	—	—	545 m	559 w-m(dp)	—	—	$\nu_a(GaC_2)$	+ $\gamma(OCN)$
—	—	544 s-m	550 vvs(p)	—	—	—	—	$\nu_s(GaC_2)$	
—	—	(544)	—	535 (sh)	529 s-m(p)			$\nu(GaO)$ (?)	
—	—	—	—	—	—	529 s-m	527 m	$\nu_a(InC_2)$	
—	—	—	—	499 s	500 vvs(p)	{495 w-m} {490 w-m}	496 vvs	$\nu_s(MC_2)$	
530 m	—	499 m	—	(499)	—	461 s-m	—		+ $\nu(OMN)$
—	501 m(p)	470 w(br)	465 m(p)	470 w	465 w(p)	—	444 w-m	$\delta(CNC)$	
—	—	—	420 vw	421 w	440 vvw	421 (sh)	—		
—	465 s-m(p)	339 s(br)	336 w(p)	—	341 w(p)	—	392 vw(br)		
327 w-m	317 vs(p)	—	—	—	—	—	—	$\delta_s(AlC_2)$	
270 w	265 w-m	(339)	—	290 s-m	287 w	275 s	280 vw	γ, $\delta(CNC)$	
—	244 w	—	—	—	—	—	244 vw		
—	—	—	212 m(p)	—	225 m(p)	—	200 w	$\delta_s(MC_2)$	
—	—	—	—	—	204 s(br)(p)	—	—		
—	166 m(dp)	—	161 w-m(dp)	—	137 s(dp)	—	117 s-m	$\gamma(MC_2)$	
—	142 (sh)(dp)	—	—	—	—	—	—		
—	115 m(dp)	—	106 m(dp)	—	102 s(dp)	—	66 m	δ(Ring)	

---

[a] Band intensities are signified by the following symbols: s, strong; m, medium; w, weak; v, very; (br), broad; (sh), shoulder. [b] CCl_4 and C_6H_6 solution (4000 - 600 cm^{-1} and 600 - 50 cm^{-1}, respectively). [c] Solid. [d] Values in brackets are also listed elsewhere in Table 7.

TABLE 8

DOMINANT VIBRATIONAL FREQUENCIES OF BIS(DIETHYLMETAL)-*N,N'*-DIMETHYLOXAMIDES (II, IV AND VI) (ν(cm^{-1}), Intensity[a])

$[(C_2H_5)_2Al]_2[O_2C_2(NCH_3)_2]$ (II)[b]		$[(C_2H_5)_2Ga]_2[O_2C_2(NCH_3)_2]$ (IV)[b]		$[(C_2H_5)_2In]_2[O_2C_2(NCH_3)_2]$ (VI)[c]		Assignment
IR	Raman	IR	Raman	IR	Raman	
—	1668 s(p)	—	1649 s(p)	—	1630 s	ν_a(OCN) in-phase
1655 vs	—	1635 vs	—	1596 vs	—	ν_a(OCN) out-of-phase
—	1451 vs(p)	—	1440 vs(p)	—	1413 vs	ν_s(OCN) in-phase
1330 s	—	1335 s	—	1280 vs	—	ν_s(OCN) out-of-phase
1002 (sh)	—	1004 s-m	—	994 m	—	$\nu(N-CH_3) + \nu(C-C)$
—	932 s(p)	—	925 m(p)	—	910 w	
849 m	838 vw	834 s-m	—	817 s-m	—	$\delta(OCN)\ (+\ \rho(CH_3-N))$
—	814 vw(dp)	810 vvw	813 w(dp)	—	808 w	
660 m	661 m-w(dp)	—	—	—	—	$\nu_a(AlC_2)$
575 (sh)	568 s(p)	(569)[d]	582 (sh)	582 m	559 m-w	$\nu_s(AlC_2)\ (+\ \delta(OCN))$
—	—	569 s-m	568 m(dp)	510 s-m	512 m	$\nu_a(MC_2)$
—	—	522 m	527 vvs(p)	465 (sh)	468 vvs	$\nu_s(MC_2)$
517 m-w	—	492 s	494 vvw	457 s	—	$\nu(OMN)$
—	498 s-m(p)	462 vw(sh)	468 vs(p)	430 (sh)	440 m	
—	464 s-m(p)	—	426 m-w(p)	—	384 w	
395 m	—	340 s-m	340 vvw	—	—	$\delta(CNC)\ (+\ \delta_s(AlC_2))$
355 vw	332 w-m(br)(p)	—	—	—	—	
304 vw	315 w-m(br)(p)	297 w-m	296 w-m(dp)	270 s	—	
—	—	278 w	271 s-m(p)	(270)	260 s-m	$\delta_s(CCM)\ (+\ \delta_s(GaC_2))$
—	198 m(dp)	—	202 (sh)(dp)	—	—	$\delta_s(InC_2) + \delta(MC_2) + \delta(Ring)$
—	—	—	186 m(dp)	—	134 m	
—	—	—	105 m(dp)	—	118 m	

[a] See Table 7, footnote *a*. [b] Spectrum taken of neat liquid. [c] Spectrum taken of solid. [d] See Table 7, footnote *d*.

a splitting of some IR bands which is not observed in the spectra of the ethyl homologues IV and VI, but this effect could also be due to crystal field distortion or to a slight twisting of the $O_2C_2N_2$ skeleton.

The IR and Raman data of bis(dimethylmetal) and bis(diethylmetal) derivatives of NMOxA are presented in Tables 7 and 8, respectively, together with the presumptive assignments. Basic vibrations of ethyl and methyl groups were omitted above 1600 cm^{-1} from Table 7, and completely from Table 8 since these frequencies do not contribute significantly to structural elucidation. For more facile band assignment, spectroscopic results from former work [5, 7, 15] were used as comparative standard.

6. Experimental

For preparation and purification of the starting alkylmetal compounds and of NMOxA we refer to the literature [3, 6].

In a 100 or 150 ml three-necked round-bottom flask with reflux condenser and "nitrogen seal" [17], the trialkylmetals dissolved in ether (Al, Ga) or benzene (Ga, In) are treated at 5-10°C with NMOxA, either in the solid state or suspended in ether or benzene. The requisite quantities of NMOxA listed in Table 9 are added batchwise (100-200 mg) under vigorous stirring. A new batch is added only after the vehement evolution of gas has subsided. To ensure complete reaction, the mixture is finally warmed to 30° or 60°C. The aluminium and gallium compounds are then isolated from the clear solutions by stripping off the solvent; the indium homologues are obtained as sparingly soluble solids.

For purification, all products are subjected to vacuum distillation or sublimation (Table 1).

For elemental analysis, C, H, and N values were obtained by the usual methods of organic combustion analysis; the metallic content was determined either gravimetrically (as metallic oxide) or by titration with titriplex III. The yields given in Table 9 always refer to *N,N'*-dimethyloxamide as the component not used in excess.

IR spectra were taken of either the neat liquids or of Nujol or Hostaflon mulls, pressed as capillary films between CsBr plates [18], and recorded with a Beckman IR 12 or a Perkin—Elmer PE 457 spectrometer. Raman spectra were measured on a PH O spectrophotometer of Coderg, Inc.; for excitation, the blue-green (4880 Å) line of an Ar laser was employed.

^{1}H NMR spectra were recorded of saturated $CDCl_3$ solutions, at 60 MHz on a Varian T-60, at 90 MHz on a Bruker HX-90 E (in CW mode). For experimental details of the ^{13}C NMR spectra, see footnote *a* to table 4.

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TABLE 9

PREPARATION AND ELEMENTAL ANALYSIS DATA FOR BIS(DIALKYLMETAL)-*N*,*N*′-DIMETHYLOXAMIDES (I-VI)

Starting materials		Product	Yield	Mol. wt.	Elemental analysis, found (calcd.) (%)			
R_3M g(mmol)	NMOxA g(mmol)		(%)		Metal	C	H	N
10.0	7.9	$[(CH_3)_2Al]_2[O_2C_2(NCH_3)_2]$	55	230.0	23.4	41.6	7.73	12.1
(138.7)	(68.0)			(228.2)	(23.65)	(42.11)	(7.95)	(12.28)
9.5	4.7	$[(C_2H_5)_2Al]_2[O_2C_2(NCH_3)_2]$	82	286.8	18.6	49.9	9.06	9.6
(83.2)	(40.5)			(284.3)	(18.98)	(50.69)	(9.22)	(9.85)
5.5	2.7	$[(CH_3)_2Ga]_2[O_2C_2(NCH_3)_2]$	92	304.7	44.3	30.3	5.74	8.8
(47.9)	(23.3)			(313.7)	(44.45)	(30.63)	(5.78)	(8.93)
4.5	2.1	$[(CD_3)_2Ga]_2[O_2C_2(NCH_3)_2]$	88	314.5	43.4	30.0	—	8.7
(36.3)	(18.1)			(325.7) (1D≙2H)	(43.62)	(30.05)	(9.46)	(8.76)
9.8	3.5	$[(C_2H_5)_2Ga]_2[O_2C_2(NCH_3)_2]$	90	372.1	37.8	39.0	7.00	7.7
(62.5)	(30.1)			(369.8)	(37.70)	(38.97)	(7.08)	(7.57)
12.2	4.3	$[(CH_3)_2In]_2[O_2C_2(NCH_3)_2]$	65	not determ.	56.2	23.5	4.42	6.75
(76.3)	(37.0)			(403.9)	(56.86)	(23.79)	(4.49)	(6.93)
14.7	4.1	$[(C_2H_5)_2In]_2[O_2C_2(NCH_3)_2]$	35	not determ.	49.4	31.3	5.69	6.15
(72.8)	(35.3)			(460.0)	(49.92)	(31.33)	(5.69)	(6.09)

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