

254. *Trimethylgallium. Part IV.*¹ *Dimethyl-gallium and -aluminium Derivatives of Some Oxy- and Thio-acids.*

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Trimethyl-gallium and -aluminium react with some carboxylic, phosphinic, thiophosphinic, and sulphinic acids, giving methane and products formulated with eight-membered rings on the basis of their molecular weights and infrared spectra. In contrast, dithiophosphinic acids give monomeric products in which the R_2PS_2 group acts as a chelate ligand. Two derivatives of trimethylindium are described, these being analogous to the gallium and aluminium compounds, but dimethylthallium dimethyldithiophosphinate is a salt. Dimethyl-aluminium and -gallium methanesulphonates are trimers in solution.

Compounds containing the dimethylgallium group have characteristic infrared absorptions at 1190—1203 ($\delta_{\text{sym}}CH_3$), 580—606 ($\nu_{\text{asym}}GaC_2$), and 533—549 cm^{-1} ($\nu_{\text{sym}}GaC_2$). The spectrum of trimethylgallium is discussed.

DIMETHYLGALLIUM acetate, from trimethylgallium and acetic acid, is dimeric in the vapour phase and in acetone solution, but when this compound was first studied² there was no opportunity to distinguish between the two likely structures, (I) and (II).

¹ Part III, Coates and Graham, *J.*, 1963, 233.

² Coates and Hayter, *J.*, 1953, 2519.

In the meantime, the presence of bridging acetate groups, as in (II), has been demonstrated by the crystal-structure analysis of several compounds and the C-O infrared stretching frequencies of these have been shown to be similar to those of ionic acetates,



both classes commonly having two strong absorptions in the range 1400—1480 and 1570—1620 cm.⁻¹, respectively.³ Dimethylgallium acetate, [H₃]acetate, and formate have strong absorptions at 1471, 1534; 1475, 1515; and 1555—1587 cm.⁻¹, respectively, in tetrachlorethylene, these being even closer together than the pairs quoted by Beattie and Gilson.³ The alternative structure, (I) would result in a strong absorption in the 1700—1750 cm.⁻¹ region. The gallium compounds therefore have the eight-membered cyclic structure (II).

Several dialkyl- and diaryl-aluminium carboxylates have been described,⁴ but neither molecular weights nor infrared spectra were reported; we would expect that these compounds, *e.g.*, Bu_{1/2}Al·OAc, also have eight-membered cyclic structures. Bridging acetate groups have been postulated to account for the polymerization of molybdenum(II) acetate,⁵ the dimerization of (π-C₆H₇)₂M·OAc (C₆H₇ = methylcyclopentadienyl, M = a lanthanide atom),⁶ and have been shown to be present in the trimethyltin acetate polymer in which acetate groups bridge planar trimethyltin groups.⁷

Chelate acetate groups are present in Zn(OAc)₂·2H₂O, in which the metal is octahedrally co-ordinated,⁸ and in Na[UO₂(OAc)₃], in which the metal and all six acetate oxygen atoms are in one plane,⁹ the O-U-O angles being only 53°. The triacetates of lanthanum and cerium(III) are monomeric in benzene,¹⁰ and in these compounds too the acetate groups are surely chelating. No example is known of a chelate acetate group bound to a tetrahedrally co-ordinated metal; presumably the valency angle strain would be excessive. Chelate acetate groups have been proposed for some boron compounds, R₂B·OAc,¹¹ but no information concerning their molecular weights has been presented. Acetoxydimethylborane (Me₂B·OAc) has very recently been found to be monomeric as vapour, and polymerized (by bridging acetate groups) in the solid state.¹²

Phosphinates, Thio-, and Dithio-phosphinates.—Similar problems arise with other oxyacids which could act as chelate groups or one- or three-atom bridging groups. Some cobalt(II) phosphinates, [(R₂PO₂)₂Co]_n, have been formulated as co-ordination polymers containing three-atom bridging phosphinate groups, Co(O-P-O)₂Co, on the basis of chemical and spectroscopic evidence.¹³ Diphenylphosphinic acid has also been regarded as a three-atom bridging group in a series of co-ordination polymers containing beryllium, chromium, and zinc.¹⁴

³ Beattie and Gilson, *J.*, 1961, 2585.

⁴ Zakharkin, Kolesnikov, Davydova, Gavrilenko, and Kamyshova, *Izvest. Akad. Nauk S.S.S.R.*, 1961, 364; Razuvaev, Mitrofanova, and Petukhov, *Zhur. Obshchei Khim.*, 1961, 31, 2340.

⁵ Bannister and Wilkinson, *Chem. and Ind.*, 1960, 319.

⁶ Maginn, Manastyrskiy, and Dubeck, *J. Amer. Chem. Soc.*, 1963, 85, 672.

⁷ Okawara, lecture at the Symposium on Organometallic Chemistry, Cincinnati, June 1963.

⁸ Talbot, *Acta Cryst.*, 1953, 6, 720.

⁹ Zachariasen and Plettinger, *Acta Cryst.*, 1959, 12, 526.

¹⁰ Misra, Misra, and Mehrotra, *J. Inorg. Nuclear Chem.*, 1963, 25, 201.

¹¹ Duncanson, Gerrard, Lappert, Pyszora, and Shafferman, *J.*, 1958, 3652; Blau, Gerrard, Lappert, Mountfield, and Pyszora, *J.*, 1960, 380.

¹² Goubeau and Lehmann, *Z. anorg. Chem.*, 1963, 322, 224.

¹³ Coates and Golightly, *J.*, 1962, 2523.

¹⁴ Block, Simkin, and Ocone, *J. Amer. Chem. Soc.*, 1962, 84, 1749; Block and Barth-Wehrenalp, *J. Inorg. Nuclear Chem.*, 1962, 24, 365; see also *Chem. and Eng. News*, 1962, July 30, p. 52.

A study of oxyacid derivatives of trimethyl-gallium or -aluminium, in which only one methyl group has been displaced, provides an opportunity to investigate the donor characteristics of the oxyacid group in simple, in contrast to polymeric, systems.

The compounds, $(\text{Me}_2\text{MO}_2\text{PR}_2)_2$ ($\text{M} = \text{Al, Ga, and, in one instance, In; R} = \text{Me, Ph}$), were prepared from the metal alkyl and the acid in ether or benzene, purified by vacuum sublimation (with difficulty, when $\text{R} = \text{Ph}$), and found to be dimeric cryoscopically in benzene.

Some of the main features of the infrared spectra of these compounds, in carbon disulphide solution (except $\text{Me}_2\text{PO}_2\text{Me}$ measured as a liquid film, and $\text{Me}_2\text{PO}_2\text{Na}$ as a fine powder¹⁵) are shown in Table I. The principal point is the separation of about 100 cm.^{-1}

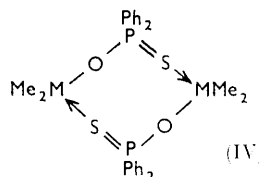
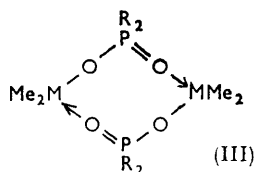
TABLE I.

Infrared spectra of phosphinates of dimethyl-aluminium, -gallium, and -indium.

Compound	$\nu(\text{P-O})$	$\delta(\text{M-CH}_3)_{\text{sym}}$	$\nu(\text{M-CH}_3)$
$(\text{Me}_2\text{AlO}_2\text{PMe}_2)_2$	1192, 1091 ^a	1192vs	682vs, 581m
$(\text{Me}_2\text{GaO}_2\text{PMe}_2)_2$	1164, 1062	1200m	588m, 538m
$(\text{Me}_2\text{InO}_2\text{PMe}_2)_2$	1171, 1057	1151s	528m, 484m
$(\text{Me}_2\text{AlO}_2\text{PPh}_2)_2$	1199, 1072	1199vs or 1188sh	683vs, 604w, 590w
$(\text{Me}_2\text{GaO}_2\text{PPh}_2)_2$	1180, 1067sh, 1048	1203s	594m, 534m
$(\text{Me}_2\text{GaO}_2\text{AsMe}_2)_2$	897, 865 ^b	1194m	580m, 535m
$\text{Me}_2\text{PO}_2\text{Me}$	1230, 1042	—	—
$\text{Me}_2\text{PO}_2^-\text{Na}^+$	1168, 1068 ¹⁵	—	—

^a All vs or s. ^b $\nu(\text{As-O})$.

between the two strong P-O absorptions. These are similar in separation and wave-number to those found in a series of salts of dimethylphosphinic acid,¹⁵ but the separation is much smaller than that of nearly 200 cm.^{-1} between the P=O and the P-O absorption in the methyl ester of dimethylphosphinic acid. We may therefore conclude, as we did in the case of acetates, that the phosphinic group acts as a three-atom bridge in the metal complexes which must have the eight-membered ring structure (III). The P-O bonds in



(III) would be equivalent, as in the ions R_2PO_2^- , and a spectroscopic similarity is to be expected. The most doubtful assignments in Table I are those of the absorptions $\delta(\text{Al-CH}_3)$, since these appear to coincide with the higher $\nu(\text{P-O})$ absorption, and there is some difficulty in distinguishing between $\nu(\text{As-O})$ in the arsenate and methyl rocking vibrations. The one dimethylarsinate examined has a pair of As-O absorptions even closer than the P-O absorptions of the phosphinates; since the compound is dimeric in benzene solution it may be assumed to have a structure similar to (III). Absorptions due to metal-methyl stretching vibrations are considered collectively later.

The monothiophosphinic acid, $\text{Ph}_2\text{P}(\text{:S})\text{OH}$, yields dimeric derivatives $(\text{Me}_2\text{MOSPh}_2)_2$ ($\text{M} = \text{Al or Ga}$), and in these there is no reason why the P-O and the P-S bonds should be equivalent, in contrast to the equivalent P-O bonds in (III). However, the infrared spectra of the aluminium and gallium compounds, which are very similar, strongly suggest structures represented by (IV), in that the phosphorus-sulphur bond appears to have an appreciably higher order than the phosphorus-oxygen bond. The main features of the spectra are given in Table 2, which includes data on other phosphorus compounds for comparison.

¹⁵ Corbridge and Lowe, *J.*, 1954, 4555.

TABLE 2.

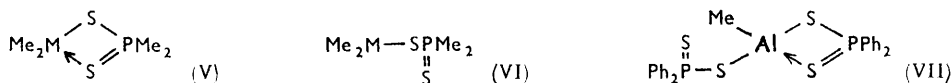
Infrared spectra of diphenylthiophosphinates of dimethyl-aluminium and -gallium.

Compound	$\nu(\text{P-O})^a$	$\nu(\text{P-S})^a$	$\delta(\text{M-CH}_3)_{\text{sym}}$	$\nu(\text{M-CH}_3)$
$(\text{Me}_2\text{AlOSPPPh}_2)_2^a$	1064, 1047	629, 612	1200m, 1189sh	678s, 568m, 548m
$(\text{Me}_2\text{GaOSPPPh}_2)_2^a$	1089, 1066	625	1199m	604s, 533s
$\text{Ph}_2\text{PS}_2\text{H}^b$	—	656, 528	—	—
$\text{Ph}_2\text{P}(\text{:S})\text{OH}^b$	892	633	—	—
$\text{Ph}_2\text{P}(\text{:S})\text{Cl}^c$	—	661	—	—

^a In CS_2 . ^b As KBr disc. ^c Liquid film. ^d All strong absorptions; Zingaro (*Inorg. Chem.*, 1963, **2**, 192) found $\nu(\text{P-S}) = 660 \text{ cm.}^{-1}$ for Ph_2PSCl , and has reviewed data on P-S and P-Se stretching frequencies.

The P-O absorptions are in the same region as the lower of the pair observed in the spectra of the phosphinates containing the PO_2 group, whereas the P-S absorptions are similar in wavenumber to those found in compounds containing the P:S double bond (compare the two acids and the chloride listed in Table 2). The aluminium compound (in benzene solution) absorbs also at 454, 403, and 355, 333 cm.^{-1} , and these absorptions could be due to vibrations having much of the character of Al-O and Al-S stretching. The gallium compound (also in benzene) has a very similar low-frequency spectrum, 426, 389 and 300, 274 cm.^{-1} , the frequencies all being displaced to lower values as would be expected for Ga-O and Ga-S vibrations.

In contrast to the phosphinates and thiophosphinates, the dithiophosphate group appears able to behave as a chelate ligand since the compounds $\text{Me}_2\text{MS}_2\text{PMe}_2$ (M = Al, Ga, or In) are all monomeric in benzene solution; the solids do not absorb trimethylamine, and must have the structure (V).



The three-co-ordinate structure (VI) is excluded by the failure of trimethylamine to add to the compound. As trimethylamine readily adds to the four co-ordinate dimers $(\text{Me}_2\text{AlSMe})_2$ ¹⁶ and $(\text{Me}_2\text{GaSR})_2$ (R = Me, aryl),² giving $\text{Me}_2\text{M}(\text{SR})\cdot\text{NMe}_3$, it would also certainly add to the co-ordinatively unsaturated (VI).

That dithiophosphinates chelate with tetrahedrally co-ordinated metals, in contrast to phosphinates and thiophosphinates, is evidently due to the ease with which sulphur undergoes valency-angle deformation relative to oxygen. That elements of the first short period resist valency-angle deformation more than heavier elements has been pointed out by Gillespie,¹⁷ who mentioned, among other examples, the cyclic silicon sulphide $\text{Me}_2\text{SiS}_2\text{SiMe}_2$ in which the Si-S-Si angle is only 75°, the lowest cyclic siloxanes containing six-membered rings with much larger valency angles.

The thallium analogue is a salt, $[\text{Me}_2\text{Tl}]^+[\text{Me}_2\text{PS}_2]^-$, both in the solid state, since its infrared spectrum is very nearly the sum of the spectra of Me_2TlBr and CsMe_2PS_2 , and in aqueous solution, as the molar conductance and the Onsager slope at 25° were appropriate for a 1:1 electrolyte, $\Lambda = 62.7 - 74.6 \text{ C}^{\frac{1}{2}}$.

The aluminium compound (V; M = Al) reacted very readily with dimethyldithiophosphinic acid, giving $(\text{Me}_2\text{PS}_2)_3\text{Al}$, also obtained from trimethylaluminium and the acid (3 mols.) in benzene solution. This may be readily purified by means of sublimation and it is monomeric in benzene solution, so that there is no reason to doubt that the aluminium is octahedrally co-ordinated.

The attempted preparation of $\text{Me}_2\text{AlS}_2\text{PPh}_2$ resulted, to our surprise, in the formation of an involatile solid of composition $\text{MeAl}(\text{S}_2\text{PPh}_2)_2$, some trimethylaluminium being left unchanged. Since the compound is monomeric in benzene and its infrared spectrum

¹⁶ Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316.

¹⁷ Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.

contains a strong absorption at 654 cm^{-1} , which can only be assigned to $\nu(\text{P}=\text{S})$, a structure (VII) is proposed, in which the metal is four co-ordinate.

The main features of the infrared spectra of the dithiophosphinates are listed in Table 3. The assignments of absorptions due to metal-sulphur vibrations (Table 3) are rather

TABLE 3.

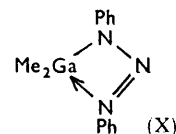
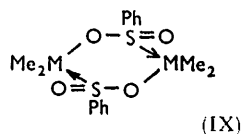
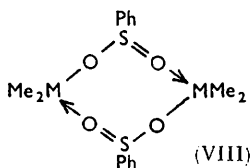
Infrared spectra of some dithiophosphinates of aluminium, gallium, indium, and thallium.

Compound	$\nu(\text{M}-\text{CH}_3)$	$\delta(\text{M}-\text{CH}_3)_{\text{sym}}$	$\nu(\text{P}-\text{S})$	$\nu(\text{M}-\text{S})$
$\text{Me}_2\text{AlS}_2\text{PMe}_2^a$	687vs, 579s	1186s, 1174sh	599s, 585s, 505s, 493m	348vs, 310m
$\text{Me}_2\text{GaS}_2\text{PMe}_2^a$	590vs, 537s	1190s	590vs?, 503s	314vs
$\text{Me}_2\text{InS}_2\text{PMe}_2^a$	508w	1147vw	596s, 496m	323sh, 313s
$(\text{Me}_2\text{PS}_2)_3\text{Al}^b$	—	—	601s, 587s, 501m	328vs, 308sh
$\text{MeAl}(\text{S}_2\text{PPh}_2)_2^a$...	673s	1182m	654s, 566vs, 485s	391s, 373sh, 329m, 312sh
$[\text{Me}_2\text{Tl}][\text{Me}_2\text{PS}_2]^c$...	540m	1170vw	588vs, 496s	—
Me_2TlBr^c	541m	1178vw	—	—
$\text{Cs}[\text{Me}_2\text{PS}_2]^c$	—	—	606vs, 505vs	—

^a Solution in CS_2 , or benzene ($<450\text{ cm}^{-1}$). ^b Nujol mull. ^c KBr disc, or Nujol mull ($<450\text{ cm}^{-1}$).

speculative on account of the paucity of relevant data, but are reasonable in view of the recent detailed analysis leading to 375 and 288 cm^{-1} for $\nu(\text{Pt}-\text{S})$ in a platinum(II) dithiocarbamate, values for $\nu(\text{Pd}-\text{S})$ being slightly higher.¹⁸ The spectra of all the dimethylphosphinates and -dithiophosphinates included two absorptions due to phosphorus-methyl stretching¹⁵ in the ranges 733 — 757 (asym) and 710 — 735 (sym) cm^{-1} , and two due to phosphorus-methyl bending¹⁹ in the ranges 271 — 299 and 256 — 283 cm^{-1} . The last were generally of medium intensity, but the salt CsMe_2PS_2 absorbed strongly at 282 and 220 cm^{-1} , the other salt, $[\text{Me}_2\text{Tl}][\text{Me}_2\text{PS}_2]$, absorbing strongly at 233 cm^{-1} with medium absorptions at 295 and 287 cm^{-1} . The suggestion¹⁹ that a sharp doublet (about 10 cm^{-1} separation) in the 1280 — 1320 cm^{-1} region is characteristic of a $\text{P}^{\text{V}}\text{Me}_2$ group ($\delta_{\text{sym}}\text{P}-\text{CH}_3$) is confirmed in all the spectra examined in the present work; the doublet was very close to 1280 and 1290 cm^{-1} in all the dimethyldithiophosphinates. The spectrum of the arsenate $(\text{Me}_2\text{GaO}_2\text{AsMe}_2)_2$ contained a similar doublet at 1259 and 1267 cm^{-1} .

Sulphinates and Sulphonates.—Tris(ethylsulphinato)aluminium, $(\text{EtSO}_2)_3\text{Al}$, has been obtained from triethylaluminium and sulphur dioxide, but its molecular weight was not reported.²⁰ Dimethylaluminium benzenesulphinate and its gallium analogue were dimeric in benzene solution, and the structure (VIII) is indicated by the infrared spectra (carbon



disulphide solution). That of the aluminium compound contained two very strong and rather broad absorptions (1027 — 1005 and 980 — 970 cm^{-1}), mainly due to sulphur-oxygen stretching vibrations, though there is some overlap with $\text{C}_{\text{ar}}-\text{H}$ in-plane deformation modes. The $\text{S}-\text{O}$ stretching vibrations of the gallium compound also resulted in very strong absorptions, identified without difficulty at 1005 and 941 cm^{-1} . These absorptions are similar in separation and wavenumber to those observed in the spectrum of potassium benzenesulphinate²¹ (1020 and 980 cm^{-1}) and of barium benzenesulphinate (986 and 960

¹⁸ Nakamoto, Fujita, Condrate, and Morimoto, *J. Chem. Phys.*, 1963, **39**, 423.

¹⁹ Halmann, *Spectrochim. Acta*, 1960, **16**, 407.

²⁰ Baker and Sisler, *J. Amer. Chem. Soc.*, 1953, **75**, 5193; see also Ziegler, Krupp, Weyer, and Larbig, *Annalen*, 1960, **629**, 251.

²¹ Detoni and Hadzi, *J.*, 1955, 3163.

cm.⁻¹, both very strong, in a potassium bromide disc). Structures such as (IX), and one in which a four-membered MO₂M ring is present, would contain sulphur-oxygen double bonds, and there would be strong absorption in the 1130 cm.⁻¹ region as observed for the ester PhSO₂Me.²¹

The two sulphonates examined, Me₂MO₃SMe (M = Al, Ga), were trimeric in benzene solution. We cannot distinguish between the six-membered cyclic structure [→ MMe₂-O(SO₂Me) →]₃, the twelve-membered ring [→ MMe₂-O-MeS(:O)-O →]₃, and less-probable structures involving metal-sulphur co-ordination, by means of infrared spectra, which are complex, as all structures contain free S=O groups. Since the compounds are trimeric, it is clear that in none of them did a sulphinate or a sulphonate group act as a chelate ligand in combination with a dimethyl-aluminium or -gallium residue.

Rather to our surprise, we obtained a dimethylgallium derivative of 1,3-diphenyltriazene, which was nearly monomeric in benzene solution (degree of association 1.12 at two concentrations). If the structure (X) is correct, the valency angles of the nitrogen atoms must be unusually small. After the present work had been completed, a brief notice²² about 1,3-diphenyltriazene derivatives of various metals appeared; most of these clearly contain the ligand chelated to an octahedrally co-ordinated metal, and there is no example in which it is shown to be chelated to a tetrahedrally co-ordinated metal. We expected our dimethylgallium compound to be dimeric, not only because of the valency angle considerations already mentioned but also by analogy with the copper(II) derivative which has an eight-membered ring.²³

Infrared Absorptions Characteristic of Dimethyl-aluminium and -gallium Groups.—Absorptions due to symmetrical and unsymmetrical stretching of the Me₂Al group have been identified at 585 and 720 cm.⁻¹, for example, in the spectrum of Me₄Al₂Cl₂,²⁴ the latter absorption being much stronger. In several of the compounds we studied, the unsymmetrical Al-CH₃ stretching absorption was obscured by bands due to aryl or other groups present, but in four compounds this was identified as a very strong absorption in the range 678—687 cm.⁻¹. The absorption due to symmetrical stretching covered a wider range, 548—604 cm.⁻¹, and was considerably weaker. In six compounds, the symmetrical deformation of the Al-CH₃ group was observed as a medium to very strong band in the narrow range 1182—1200 cm.⁻¹.

Absorptions due to gallium-methyl stretching were identified in thirteen compounds containing the Me₂Ga group; that due to the unsymmetrical mode was the stronger and within the range 580—606 cm.⁻¹, that due to the symmetrical mode being assumed to occur at lower frequencies by analogy with spectra of aluminium compounds (and in view of the spectrum of trimethylgallium, see below), being in the range 533—549 cm.⁻¹. The symmetrical deformation of the Ga-CH₃ group resulted in a medium to strong absorption in the range 1190—1203 cm.⁻¹.

The spectrum of trimethylgallium vapour (10 cm. cell, 15 mm. pressure), observed in the range 420—2000 cm.⁻¹, was remarkable in that the Ga-CH₃ unsymmetrical deformation resulted in a very weak broad band centred on 1408 cm.⁻¹, whereas the absorptions due to a symmetrical deformation were a strong triplet (PQR) at 1212, 1205, and 1198 cm.⁻¹. The other features were three strong absorptions at 769, 735, and 727 cm.⁻¹, no doubt due to methyl rocking vibrations, and a very strong triplet at 587, 583, and 575 cm.⁻¹ in the region in which the unsymmetrical GaMe₂ stretching mode was observed in the other compounds. The gallium-methyl symmetrical vibration would be infrared-inactive if the GaC₃ framework were planar, and no absorption was observed between 570 and 420 cm.⁻¹ (the limit of the instrument).

²² Brinckman and Haiss, *Chem. and Ind.*, 1963, 1124.

²³ Brown and Dunitz, *Acta Cryst.*, 1961, **14**, 480.

²⁴ Hoffmann, *Z. Elektrochem.*, 1960, **64**, 616; Gray, *Canad. J. Chem.*, 1963, **41**, 1511.

EXPERIMENTAL

Nearly all the compounds studied are sensitive to air or moisture and were handled at all times in vacuum or under an atmosphere of purified nitrogen. Aluminium, gallium, and indium were determined as their 8-hydroxyquinoline complexes. Hydrolysable methyl, present in dimethylaluminium compounds, was determined by measurement, in a conventional apparatus for quantitative gas-handling, of methane evolved after hydrolysis with 2-methoxy-ethanol and dilute sulphuric acid. The methyl content of dimethylgallium compounds could not be determined in this way since hydrolysis proceeds to completion only under extreme conditions, and then only slowly.

Infrared spectra were recorded with a Grubb-Parsons GS2A prism-grating spectrometer between 5 and 23 μ , and a DB3/DM2 200-line per cm. grating spectrometer between 21 and 50 μ . Compounds were commonly examined in carbon disulphide solution between 7 and 23 μ , and in benzene solution or as Nujol mulls between 16 and 50 μ . Spectra listed below are for carbon disulphide or benzene solution, except when stated otherwise. Molecular weights were measured cryoscopically in benzene at the stated concentrations in parentheses.

Preparations.—Nearly all the compounds were prepared by slow addition of the acid, either suspended or, more commonly, dissolved in benzene, to a little more than one mol. of the trimethyl derivatives of the metal. The reaction product remained dissolved in the solvent, which was then removed under reduced pressure. The product was in all cases [except (VII) and the compounds described as salts] purified by vacuum sublimation, at the temperatures and pressures stated.

Dimethylgallium acetate(II), m. p. 162—163° (lit.,² 162.0—162.3°), after sublimation at 90—95°/0.01 mm., absorbed at 1754w, 1534vs, 1471vs, 1408vs, 1203s, 1053m, 1030ms, 965m, 761sh, 740s, 695vs, 612m, 601s, 549ms, 513m, 329m (in C₂Cl₄ for carbonyl region, otherwise in Nujol mull).

Dimethylgallium [²H₃]acetate, from trimethylgallium and [²H₄]acetic acid, m. p. 164—165°, after sublimation at 100—110°/0.01 mm. absorbed (C₂Cl₄ and Nujol mull) at 1754w, 1515vs, 1475vs, 1447s, 1203s, 1092w, 1055m, 1029ms, 929ms, 918ms, 841s, 758sh, 735vs, 696ms, 661vs, 600vs, 548ms, 526m, 471w, 314m.

Dimethylgallium formate, (Me₂GaO₂CH)₂, m. p. 97—98° after sublimation at 60°/0.01 mm. [Found: Ga, 48.1, *M* (0.2, 0.3 wt. %), 312, 312. C₆H₁₄Ga₂O₄ requires Ga, 48.2%, *M*, 290]. Infrared spectrum: (C₂Cl₄ and Nujol mull) 1616vs, 1587vs, 1555vs, 1377vs, 1353vs, 1206ms, 1202ms, 1192ms, 823s, 738vs, 720sh, 699sh, 606s, 549m, 382m.

Dimethylaluminium dimethylphosphinate, (III; M = Al, R = Me), m. p. 43° after sublimation at 100°/0.01 mm. [Found: Al, 18.0; hydrolysable methyl, 19.8; *M* (0.90, 1.36, 1.47 wt. %), 313, 333, 332. C₈H₂₄Al₂O₄P₂ requires Al, 18.0; hydrolysable methyl, 20.0%; *M*, 300]. Infrared spectrum: 1428sh, 1316s, 1307s, 1192vs, 1091vs, 935w, 878s, 757m, 728m, 682vs, 581m.

Dimethylgallium dimethylphosphinate, (III; M = Ga, R = Me), m. p. 54° after sublimation at 80°/0.01 mm. [Found: Ga, 36.1; *M* (1.32, 1.98, 2.16 wt. %), 389, 375, 370. C₈H₂₄Ga₂O₄P₂ requires Ga, 36.2%, *M*, 385]. Infrared spectrum: 1300m, 1294m, 1200m, 1164vs, 1112w, 1062vs, 923vw, 870vs, 747m, 735m, 588m, 538m, 483m, 439m, 299w, 283w.

Dimethylindium dimethylphosphinate, (III; M = In, R = Me), m. p. 75—76° after sublimation at 60—65°/0.01 mm. [Found: In, 48.2; hydrolysable methyl, 12.5; *M* (1.13, 1.69 wt. %), 474, 480. C₈H₂₄In₂O₄P₂ requires In, 48.3; hydrolysable methyl, 12.6%; *M*, 475.5]. Infrared spectrum: 1418sh, 1299m, 1292m, 1171vs, 1151s, 1121w, 1057vs, 920vw, 866s, 742m, 713m, 528m, 484m.

Dimethylaluminium diphenylphosphinate, (III; M = Al, R = Ph), m. p. 153—156° after sublimation at 160°/0.01 mm. [Found: Al, 9.8; hydrolysable methyl, 10.9; Ph₂PO₂ as Ph₂PO₂H, 79.7; *M* (0.59, 0.89 wt. %), 527, 527. C₂₈H₃₂Al₂O₄P₂ requires Al, 9.85; hydrolysable methyl, 10.95; Ph₂PO₂, 79.6%; *M*, 548]. Infrared spectrum: 1431vs, 1199vs, 1188sh, 1134vs, 1072vs, 1027m, 998m, 922vw, 785vw, 752s, 730s, 691vs, 683vs, 620vw, 604w, 590w, 548m.

Dimethylgallium diphenylphosphinate, (III; M = Ga, R = Ph), m. p. 164° after sublimation at 160°/0.01 mm. [Found: Ga, 21.9; Ph₂PO₂ as Ph₂PO₂H, 68.3; *M* (1.25, 1.89, 2.06 wt. %), 667, 646, 642. C₂₈H₃₂Ga₂O₄P₂ requires Ga, 22.0; Ph₂PO₂, 68.8%, *M*, 633.5]. In contrast to its aluminium analogue, this required treatment with hot concentrated hydrochloric acid for complete hydrolysis for diphenylphosphinic acid determination. Infrared spectrum: 1431vs, 1203ms, 1180s, 1130vs, 1067sh, 1048s, 1024ms, 998m, 751ms, 727s, 700sh, 692s, 594m, 564ms, 534m.

Dimethylaluminium diphenylthiophosphinate, (IV; M = Al), m. p. 227—228° after sublimation at 160—180°/ < 0.01 mm. [Found: Al, 9.2; hydrolysable methyl, 10.2; M (0.90, 1.40 wt. %), 597, 564. $C_{28}H_{32}Al_2O_2P_2S_2$ requires Al, 9.3; hydrolysable methyl, 10.35%; M, 580]. Infrared spectrum: 1439vs, 1200m, 1189sh, 1117s, 1064s, 1047ms, 1026ms, 999m, 800m, 750s, 746sh, 727vs, 715vs, 691vs, 678sh, 656sh, 629ms, 612ms, 568m, 548m, 517vs, 454m, 403m, 355s, 333ms.

Dimethylgallium diphenylthiophosphinate, (IV; M = Ga), m. p. 203—204° after sublimation at 160—180°/ < 0.01 mm. [Found: Ga, 20.9, M (1.20, 1.70 wt. %), 664, 676. $C_{28}H_{32}Ga_2O_2P_2S_2$ requires Ga, 20.9%, M, 666]. Infrared spectrum: 1431vs, 1199m, 1089s, 1066s, 1027ms, 999m, 751s, 745sh, 720vs, 707vs, 692vs, 676m, 625s, 604vs, 533sh, 523vs, 509sh, 426m, 389m, 300vs, 274w.

Dimethylaluminium dimethyldithiophosphinate, (V; M = Al), m. p. 103—104° after sublimation at 40—45°/0.01 mm. [Found: Al, 14.5; hydrolysable methyl, 16.3; M (0.98, 1.47 wt. %), 218, 206. $C_4H_{12}AlP_2S_2$ requires Al, 14.8; hydrolysable methyl, 16.5%; M, 182]. Infrared spectrum: 1414s, 1403s, 1395ms, 1296m, 1287s, 1186s, 1174w,sh, 991w, 948vs, 912vs, 853s, 762s, 740s, 729s, 687vs, 646ms, 599ms, 585ms, 579ms, 505s, 493m, 394w, 348vs, 310m, 292vw, 271m.

Methylaluminium bisdiphenyldithiophosphinate, (VII), softened at 180° and melted at 260° [Found: Al, 4.6; hydrolysable methyl, 2.80, M (1.0, 1.5 wt. %), 560, 541. $C_{25}H_{23}AlP_2S_4$ requires Al, 5.0; hydrolysable methyl, 2.80%; M, 540.5]. Infrared spectrum: 1437s, 1385vw, 1337vw, 1307w, 1182m, 1160vw, 1105s, 1101s, 1068vw, 1028m, 1000m, 985vw, 960vw, 920vw, 813w, 785w, 744s, 709vs, 689vs, 673s, 654s, 633sh, 612m, 566vs, 529w, 485s, 391s, 373sh, 329m, 312sh, 230m.

Trisdimethyldithiophosphinatoaluminium, from trimethylaluminium and dimethyldithiophosphinic acid (2.9 mols.) in benzene, m. p. 186—188° after sublimation at 190°/0.01 mm. [Found: Al, 6.6, M (0.97, 1.40 wt. %), 429, 441. $C_8H_{18}AlP_3S_6$ requires Al, 6.7%; M, 403]. Infrared spectrum: (Nujol mull) 1290vw,sh, 1280m, 1160vw, 956s, 944s, 921s, 909s, 858w, 847m, 741sh, 729s, 601s, 587ms, 501m, (benzene solution) 328vs, 308s, 272m, 264m.

Dimethylgallium dimethyldithiophosphinate, (V; M = Ga), m. p. 153—154° after sublimation at 100°/0.01 mm. [Found: Ga, 30.9; M (0.93, 1.39 wt. %), 247, 247. $C_4H_{12}GaP_2S_2$ requires Ga, 31.0%; M, 225]. Infrared spectrum: 1418s,sh, 1406s,sh, 1397ms, 1292m, 1282ms, 1190ms, 944vs, 908vs, 850s, 761ms, 735s,sh, 725vs, 590vs, 537ms, 503s, 314vs, 277m,sh, 267s,

Dimethylindium dimethyldithiophosphinate, (V; M = In), m. p. 184—185° after sublimation at 110—120°/0.01 mm. [Found: In, 42.5; M (0.49, 0.74 wt. %), 291, 293. $C_4H_{12}InP_2S_2$ requires In, 42.5%; M, 270]. Infrared spectrum: 1416ms,sh, 1406m,sh, 1397m, 1294w, 1284m, 1147vw, 948s, 911s, 898w,sh, 852m, 738m, 724ms, 596s, 508w, 496ms, 323m, 313s, 271m, 256m.

Dimethylthallium dimethyldithiophosphinate, $[Me_2Tl]^+[Me_2PS_2]^-$, was precipitated when dimethyldithiophosphinic acid in ethanol was added to an aqueous solution of dimethylthallium cyanide,²⁵ decomp. from 185°, becoming black at ca. 200° (Found: C, 13.3; H, 3.4. $C_4H_{12}PS_2Tl$ requires C, 13.4; H, 3.3%). The salt is insoluble in benzene, slightly soluble in water, and may be crystallized from ethanol. Infrared spectrum: (KBr disc) 1404m, 1290vw, 1280ms, 1170vw, 1087vw, 943vs, 909vs, 847m, 797s, 733m, 710s, 588vs, 540m, 496ms, (Nujol mull) 295m, 287w,sh, 233ms.

Cæsium dimethyldithiophosphinate, from cæsium carbonate and the acid, was crystallized from ethanol-water. (Found: C, 9.3; H, 2.5. $C_2H_6CsPS_2$ requires C, 9.3; H, 2.3%). Infrared spectrum: (KBr disc) 1418m, 1404ms, 1290m, 1279s, 1105vw, 952s, 915vs, 847s, 734s, 715vs, 606vs, 505vs, (Nujol mull) 282s, 220s.

Dimethylaluminium benzenesulphinate, (VIII; M = Al), m. p. 61—62° after sublimation at 120—130°/0.01 mm. [Found: Al, 13.4; hydrolysable methyl, 7.5; M (0.74, 1.09 wt. %), 429, 429. $C_{16}H_{22}Al_2O_4S_2$ requires Al, 13.6; hydrolysable methyl, 7.6%; M, 396]. Infrared spectrum: 1445s,sh, 1192ms, 1089m, 1027—1005s,br, 980—970s,br, 753s, 704vs, 688vs, 620m, 612w, 588w.

Dimethylgallium benzenesulphinate, (VIII; M = Ga), m. p. 56—57° after sublimation at 120°/0.01 mm. [Found: Ga, 28.8; M (0.77, 1.13 wt. %), 495, 477. $C_{16}H_{22}Ga_2O_4S_2$ requires Ga, 28.9%; M, 482]. Infrared spectrum: 1445s, 1203s, 1124m, 1048m, 1005vs, 941s, 735s, 697s, 683s, 584s, 539s, 459s, 420s, 352s, 329m,sh, 275w.

²⁵ Coates and Mukherjee, *J.*, 1963, 229.

*Barium benzenesulphinat*e, from the carbonate and the acid, was crystallized from water (Found: C, 34.2; H, 2.5. $C_{12}H_{10}BaO_4S_2$ requires C, 34.35; H, 2.4%). Infrared spectrum: (KBr disc) 1443ms, 1088m, 1020m,sh, 986vs, 971s, 960vs, 751m,sh, 744s, 704ms, 689s, 581s, 505ms, 487m.

Dimethylaluminium methanesulphonate, $(Me_2AlO_3SMe)_3$, m. p. 65–66° after sublimation at 100°/0.01 mm. [Found: Al, 17.7; hydrolysable methyl, 19.6; *M* (0.74, 1.11 wt. %), 432, 467. $C_9H_{27}Al_3O_9S_3$ requires Al, 17.7; hydrolysable methyl, 19.8%; *M*, 456]. It is only sparingly soluble in carbon disulphide.

Dimethylgallium methanesulphonate, $(Me_2GaO_3SMe)_3$, m. p. 79–80° after sublimation at 100°/0.01 mm. [Found: Ga, 35.7; *M* (0.67, 1.01 wt. %), 587, 587. $C_9H_{27}Ga_3O_9S_3$ requires Ga, 35.8%; *M*, 584].

Dimethylgallium dimethylarsinate, $(Me_2GaO_2AsMe_2)_2$, m. p. 144–145° after sublimation at 110°/0.01 mm. [Found: Ga, 29.8; *M* (1.08, 1.60 wt. %), 475, 502. $G_8H_{24}As_2Ga_2O_4$ requires Ga, 29.9%; *M*, 473]. Infrared spectrum: 1267m, 1259w, 1194m, 897s, 884vs, 865s, 818m, 738ms, 725ms, 675vs, 642m, 580m, 535m, 433s, 408s, 283ms, 269m.

1,3-Diphenyltriazenodimethylgallium, (X), brown-yellow, m. p. 53–55° after sublimation at 100°/0.01 mm. [Found: Ga, 23.3; *M* (1.6, 2.5 wt. %), 332, 332. $C_{14}H_{16}GaN_3$ requires Ga, 23.6%; *M*, 296]. The infrared spectrum was complicated up to 15 μ but GaC_2 absorptions were easily identified at 595 and 545 cm^{-1} .

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