GALLIUM AND INDIUM

ANNUAL SURVEY COVERING THE YEAR 1978

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Introduction and Reviews

Studies on organogallium and —indium chemistry during 1978 have continued at about the same rate as those in 1977.* This survey describes these in the order of 1) reviews, 2) synthesis (including one patent), reactions, structure, and bonding, 3) analysis and phase diagrams, and 4) applications.

Reviews on 'Group III Elements: Al, Ga, In, and Tl (in organometallic chemistry)' with 103 references and a bibliography [1] and on 'X-Ray Crystal and Molecular Structures of Compounds Containing B, Al, Ga, In, and Tl' with 56 references [2] were published.

Synthesis, Reactions, Structure, and Bonding

A detailed mathematical model based on enthalpies, for the formation of $(CH_3)_3Ga$ from $GaCl_3$ and $(CH_3)_3Al$, was developed by Russian chemists [3].

Dimethylpropynylmetal compounds, $(CH_3)_2MC \equiv CCH_3$ (M = Al, Ga, and In), were prepared in 40—60% yield by the reaction of $(CH_3)_2MX$ (X = Cl and Br) with $NaC \equiv CCH_3$. These compounds (mp: 49—51, 50—51, and 101—103°C for M = Al, Ga, and In, respectively) are dimeric in nondonor organic solvents. Infrared, Raman, $^1H$ NMR, and $^{13}C$ NMR spectra of the compounds were discussed, although their structures have not been clarified by these techniques. An X-ray structure analysis was performed for the In derivative; it crystallizes in the orthorhombic space group Pnma with four formula units per unit cell. The structure involves the In atom placed in a slightly distorted trigonal bipyramid, as seen in Fig. 1; a center ($e.g.$ M') of the C≡C bond of neighbouring molecules occupies an apical position of the trigonal bipyramid. The In—M' distance (2.899 Å) is evidently shorter than the In—$C_3$' (2.933 Å) and In—$C_4$' (2.989 Å) distances. The same configuration has been suggested for the Ga compound on the basis of the ν(C≡C) frequency being close to that of the In analogue [4].

Trimethylgallium and —indium react with $O_2$ to give dimethylmetal peroxides, $(CH_3)_2MOOCH_3$ (M = Ga, In), in quantitative yields. Thermolysis of the Ga perox-

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* T. Tanaka, Gallium and Indium, Annual Survey Covering the Year 1977,

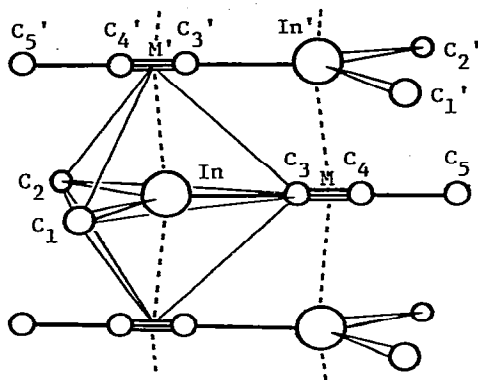   *J. Organometal. Chem.*, 158 (1978) 211.

Fig. 1.    Structure of $(CH_3)_2InC\equiv CCH_3$

ide in nonane at 120°C for 3 hr gave $CH_3GaO$ (50%), $(CH_3)_2GaOH$ (25%), $(CH_3)_2Ga-OCH_3$ (11%), $CH_3Ga(OCH_3)_2$ (11%), $(CH_3)_2GaO(CH_2)_8CH_3$ (4.6%), $CH_4$ (64%), and $CH_3OH$ (63%).    However, there is no description on the structure or properties of $CH_3GaO$.    Similar $t$-butyl peroxides, $(CH_3)_2MOOC(CH_3)_3$ (M = Ga, In), also were obtained quantitatively by the solvolysis of $(CH_3)_3M$ with $(CH_3)_3COOH$, and their thermolyses were examined [5].

The reaction of $R_3M$ (R = $CH_3$ and $C_2H_5$, M = Al and Ga; R = $CH_3$, M = In) with N,N'-dimethylacetamidine, $HN(CH_3)C(=NCH_3)CH_3$, yields compounds with the formula $R_2M(NCH_3)_2CCH_3$, which exist as dimers in solution.    Infrared and Raman spectra of these compounds have suggested that the $M_2N_4C_2$ skeletons are centrosymmetric packered eight-membered ring, probably with $C_{2h}$ symmetry, as depicted in Fig. 2; a or b [6].    The dimethylaluminum and -gallium derivatives, $[(CH_3)_2M(NCH_3)_2C-$
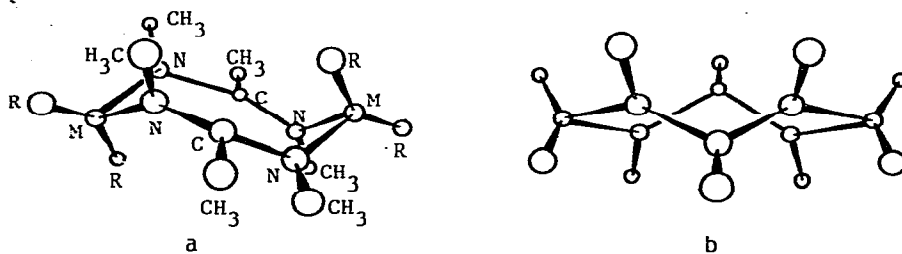


Fig. 2.    Possible configurations of $[R_2M(NCH_3)_2CCH_3]_2$: M = Al, Ga, or In; R = $CH_3$ or $C_2H_5$.

$CH_3]_2$, were studied by X-ray crystallographic analysis, which has demonstrated that they assume a chair-like form (a in Fig. 2) [7]; both the compounds crys-tallize in the monoclinic space group $P2_1/c$ with two dimers per unit cell.    The structure for the Ga compound was refined to R = 0.056.    The mean bond lengths of Ga–N and N–C within the ring are 1.979 and 1.335 Å, respectively.    The exo-

cyclic mean bond lengths of Ga–C, N–C, and C–C are 1.998, 1.484, and 1.507 Å, respectively. The Ga atom is tetrahedrally coordinated and the distortion is only slight.

Trimethylgallium also reacts with N,N'-dimethyloxamide to afford two isomeric N,N'-bis(dimethylgallium)-N,N'-dimethyloxamide complexes (Eq. 1), which were characterized by X-ray crystal analysis as adopting *cis* and *trans* configurations with respect to the central oxamide C–C bond, as shown in 1 and 2, re-

$$(CH_3)_3Ga \quad + \quad \begin{matrix} OC-NHR \\ | \\ OC-NHR \end{matrix} \quad \xrightarrow{-2CH_4} \quad (CH_3)_2Ga(RN-COCO-NR)Ga(CH_3)_2 \qquad (1)$$

$$R = H, \ CH_3$$



1: $C_{2h}$                2: $C_{2v}$

spectively. The ratio of isomers formed is dependent on the reaction conditions. Infrared and Raman spectra of the *cis* and *trans* isomers also were assigned in detail, especially in the Ga–C, Ga–O, and Ga–N frequency regions [8].

Dimethylgallium tetrahydroborate (mp: *ca.* 1°C) was synthesized by the following two reactions in the absence of a solvent at –15°C. The latter was

$$(CH_3)_3Ga \quad + \quad B_2H_6 \quad \longrightarrow \quad (CH_3)_2GaBH_4 \quad + \quad \tfrac{1}{2}(CH_3BH_2)_2 \qquad (2)$$

$$(CH_3)_2GaCl \quad + \quad LiBH_4 \quad \longrightarrow \quad (CH_3)_2GaBH_4 \quad + \quad LiCl \qquad (3)$$

the more satisfactory method. The compound obtained was characterized by molecular weight, mass, infrared, and ^{1}H NMR spectra, as well as elemental analysis [9]. The infrared spectrum in the gaseous state is consistent with a molecular model $(CH_3)_3Ga(\mu-H)_2BH_2$ having $C_{2v}$ symmetry with four coordinate Ga linked to a bidentate $BH_4$ group (3). Such a structure, however, appears to persist in the condensed phase, increasing polarization in the sense $[(CH_3)_2Ga]^+$–$[BH_4]^-$. Dimethylgallium tetrahydroborate is thermally much less stable than the Al analogue; gaseous $(CH_3)_2GaBH_4$ at a pressure of *ca.* 10 mmHg decomposes with a half-life of the order of 3 hr at room temperature. The decomposition proceeds *via* an initial intra- and intermolecular exchange process shown in Scheme 1.

Trialkylgalliums are known to react with compounds containing 'active

Scheme 1



3

hydrogen', eliminating alkane to yield either four- or five-coordinate gallium compounds [e.g. see K. S. Chong et al., *Can. J. Chem.*, 55 (1977) 2540], which frequently occur as dimers. Thus, L-prolinatodimethyl- and -diethylgallium (4) were obtained by the reaction of $R_3Ga$ ($R = CH_3$, $C_2H_5$) with L-proline in refluxing



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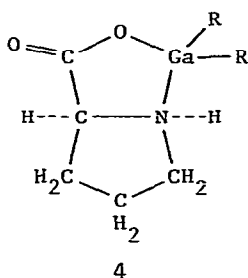
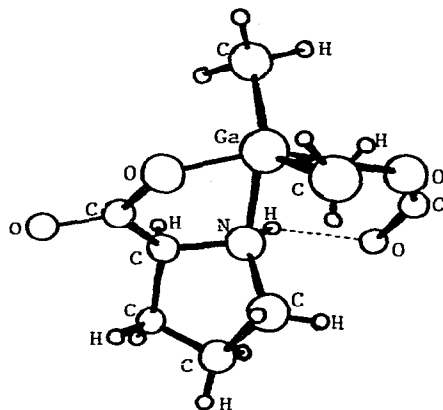benzene [10]. The dimethylgallium derivative crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. The crystal structure consists of molecules



Fig. 3. The unique part of the L-prolinato-
dimethylgallium structure.

each of which is linked to two others by weak Ga-O bonds and N-H··O hydrogen bonds to form a chain-like polymeric structure. As illustrated in Fig. 3, the

Ga atom is five coordinate and has distorted trigonal bipyramidal geometry. Important bond lengths are: Ga-O(axial), 2.044(3) and 2.695(3); Ga-N, 2.035(3); and Ga-C, 1.924(5) and 1.958(5) Å.   It also was reported in a patent [11] that $(CH_3)_3M$ (M = Al, Ga, In, Tl) react with $(CH_3)_3P=NP(=CH_2)(CH_3)_2$ to give double ylide dimethylmetal complexes shown in 5.
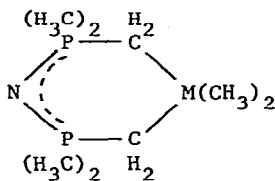


5: M = Al, Ga, In, Tl

Methylgallium diacetate, $CH_3Ga(OOCCH_3)_2$, was prepared by the reaction of $(CH_3)_3Ga$ with $CH_3COOH$ in a 1/2 mole ratio.   The structure was determined by vibrational spectroscopy and X-ray analysis [12].   The methylgallium compound crystallizes in the monoclinic space group $P2_1/c$ with eight formula units per unit cell.   The monomers are linked together by acetate groups, forming poly- meric layers.   Beside the bridging acetate, there are also 'free' acetate groups coordinated at the distorted trigonal bipyramidal coordinated Ga(1), as depicted in Fig. 4; the Ga(2) atom is coordinated distorted tetrahedrally and the acetate groups bonded to Ga(2) are all bridging.
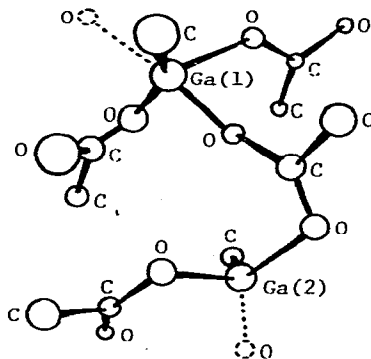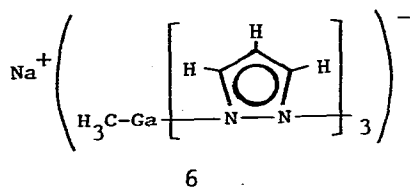


Fig. 4.   The structure of $CH_3Ga(OOCCH_3)_2$

Methylgallium dichloride reacted with sodium pyrazolide, $Na^+(N_2C_3H_3)^-$, in tetrahydrofuran to yield sodium methyltris(1-pyrazolyl)gallate (6).   This anion acts as a tridentate ligand to bivalent transition metal ions, giving complexes of the $[CH_3Ga(N_2C_3H_3)_3]_2M$ type (M = Mn, Fe, Co, Ni, Cu, Zn), which may possess an octahedral $MN_6$ core.   The ligand forms also a variety of metal carbonyl complexes.   Its coordination ability in Mo, W, and Mn carbonyl derivatives was

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$$Na^+ \left( \left[ H_3C-Ga \left[ \begin{array}{c} H \\ H \diagup \diagdown H \\ N-N \end{array} \right]_3 \right] \right)^-$$

6

compared with that of the analogous borate ligand. Infrared and bond length data have suggested that the gallate ligand is superior in creating an electron-rich transition metal center and also affords greater steric protection for the metal center. The tridentate chelate nature of the ligand has been demonstrated by the crystal structure analysis of $[CH_3Ga(N_2C_3H_3)_3]Mo(CO)_2(\eta^3-C_3H_5)$ [13]. The structure is shown in Fig. 5.
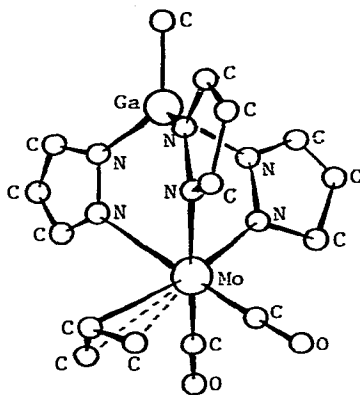


Fig. 5. The structure of $[CH_3Ga(N_2C_3H_3)_3]Mo(CO)_2(\eta^3-C_3H_5)$

Sodium and potassium tetrahydrogallates were reported to react with 1-alkynes *via* metalation to give tetraalkynylgallates or *via* addition to give tetraalkenylgallates, as shown in Scheme 2 [14]. The reactions were examined

Scheme 2

$$MGaH_4 + 4HC\equiv C(CH_2)_4R \begin{array}{c} \nearrow MGa[C\equiv C(CH_2)_4R]_4 + 2H_2 \\ \searrow MGa[CH=CH(CH_2)_4R]_4 \end{array}$$

$$M = Na, K; \quad R = H, CH_3, C_2H_5.$$
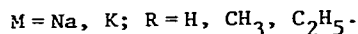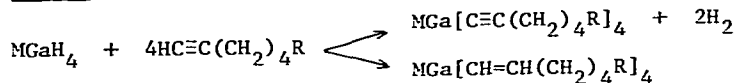
under the following various conditions; (i) with or without a solvent, such as diglyme, tetrahydrofuran, and toluene, (ii) in the presence or absence of an additive, such as $(C_2H_5)_2NH$ and $(C_2H_5)_3Ga$, and (iii) at 65°C or 100°C. The main product in the reactions was $MGa[C\equiv C(CH_2)_4R]_4$ irrespective of the reaction

conditions.    In the $NaGaH_4-HC\equiv CC_6H_5$ system in diglyme or in tetrahydrofuran, however, the addition reaction proceeds in preference to the metalation reaction. In all the reactions, $MGaH_4$ are less active than $MAlH_4$.

Vibrational spectra of tetramethyl compounds of the Group III elements, $X^+[M(CH_3)_4]^-$ ($M = Al$, $X = K$ and $P(CH_3)_4$; $M = Ga$, $X = As(CH_3)_4$; $M = In$, $X = Na$, As-$(CH_3)_4$, and $Sb(CH_3)_4$), have been assigned in detail.    Thus, a set of comparable force constants for the tetramethyl compounds of Al, Si, P/Ga, Ge, As/In, Sn, Sb were obtained using a new procedure for determination of force constants [15].

## Analysis and Phase Diagrams

Retention volumes in gas chromatography were given as functions of the boiling points of $(C_2H_5)_3M$ ($M = B$, Al, Ga, In, Tl) as well as ethyl compounds of the Group IV to VII elements [16].    It also was reported that the decomposition of alkyl derivatives of the Group III elements during chromatographic analysis can be minimized by using $H_2O-$ and $O_2-$free He carrier gas and by depositing a Cr film on a surface of chromaton N support [17].    The Cr film was deposited by thermal decomposition of the products of bis(ethylbenzene)chromium synthesis at 350-400°C.

A phase diagram of the $(CH_3)_3Ga-(C_2H_5)_3As$ system was obtained by differential thermal analysis [18].    The system contains one congruently melting compound of an equimolar composition.    A smoothed maximum observed on the liquidus curve corresponding to the chemical compound has indicated its partial dissociation in the liquid state.

## Applications

Several organometal(III) dithiocarbamates of the formula $R_nM(S_2CNR'_2)_{3-n}$ ($M = Ga$, In, or Tl; $R = C_6H_5$ or $CH_2C_6H_5$; $R' = $ alkyl or aryl; $n = 1$ or 2) were evaluated *in vitro* against five fungi and four bacteria [19].    Of these, $(C_6H_5)_2GaS_2CN(C_2H_5)_2$ has the best antimicrobial activity.

Epitaxial films, such as with thickness of $<0.2$ μ, of single crystal gallium arsenide are useful for microwave device applications.    Thus, a new technique for epitaxial growth of such ultrathin films on single crystal Si or Ge was developed by a chemical vapor deposition flow process with $(CH_3)_3Ga-AsH_3-H_2$ mixtures (total pressure ($P$), 40-100 torr; $H_2$ and $AsH_3$ partial pressures, 25-76 and 0.5-2.0 torr, respectively) at 520-750°C [20].    For given values of $P$, $H_2$ flow rate, $AsH_3$ concentration, and temperature, the GaAs film growth rate increased linearly with increasing $(CH_3)_3Ga$ concentration.    Effects of the $H_2$ and $AsH_3$ concentrations and temperature on growth of the film also were examined. The films thus obtained were evaluated by crystallographic studies, impurity analyses, photoluminescence and Hall-effect measurements, and test performance in several devices.    On the other hand, kinetics of the chemical vapor deposition of GaAs from $(CH_3)_3Ga$ and $AsH_3$ in a $H_2$ carrier gas was studied and a mass

transport model for the reactor has been presented to serve as a basis for comparison of experimental data with kinetic models for the growth process [21]. Morphology of GaAs epitaxial layers grown in the $(CH_3)_3Ga-AsH_3-H_2$ system also was reported [22].

## References

1. J. P. Maher, *Organometal. Chem.*, 6 (1976) 78 (Pub. 1978).

2. M. B. Hursthouse, *Mol. Struct. Diffr. Methods*, 5 (1977) 382; *Chem. Abstr.*, 88 (1978) 180350n.

3. K. K. Fukin, A. M. Kut'in, and I. A. Frolov, *Zh. Obshch. Khim.*, 47 (1977) 2410; *Chem. Abstr.*, 88 (1978) 50110y.

4. W. Fries, W. Schwarz, H. D. Hausen, and J. Weidlein, *J. Organometal. Chem.*, 159 (1978) 373.

5. Yu. A. Aleksandrov, N. V. Chikinova, G. I. Makin, N. V. Kornilova, and V. I. Bregadze, *Zh. Obshch. Khim.*, 48 (1978) 467; *Chem. Abstr.*, 89 (1978) 6352a.

6. F. Gerstner and J. Weidlein, *Z. Naturforsch.*, 33B (1978) 24.

7. H. D. Hausen, F. Gerstner, and W. Schwarz, *J. Organometal. Chem.*, 145 (1978) 277.

8. P. Fischer, R. Graf, and J. Weidlein, *J. Organometal. Chem.*, 144 (1978) 95.

9. A. J. Downs and P. D. P. Thomas, *J. Chem. Soc., Dalton*, (1978) 809.

10. K. R. Breakell, S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, 55 (1977) 4174.

11. H. Schmidbaur and H. J. Fueller, *Ger. Offen.*, (1978) 2,701,143; *Chem. Abstr.*, 90 (1979) 23243d.

12. H. D. Hausen, K. Sille, J. Weidlein, and W. Schwarz, *J. Organometal. Chem.*, 160 (1978) 411.

13. K. R. Breakell, S. J. Rettig, D. L. Singbell, A. Storr, and J. Trotter, *Can. J. Chem.*, 56 (1978) 2099.

14. V. V. Gavrilenko, V. S. Kolesov, Yu. N. Smirnov, and L. I. Zakharkin, *Zh. Obshch. Khim.*, 48 (1978) 2067; *Chem. Abstr.*, 90 (1979) 38983u.

15. G. Tatzel, H. Schrem, and J. Weidlein, *Spectrochim. Acta*, 34A (1978) 549.

16. I. Tohyama and K. Otozai, *Z. Anal. Chem.*, 288 (1977) 286.

17. A. D. Zorin, V. K. Vanchagova, V. A. Umilin, and N. M. Sorokina, *Zavod. Lab.*, 44 (1978) 22; *Chem. Abstr.*, 89 (1978) 36146d.

18. E. B. Sokolov, B. K. Skachkov, E. A. Efremov, B. I. Kozyrkin, A. P. Ferapontov, and V. A. Fedorov, *Zh. Fiz. Khim.*, 52 (1978) 798; *Chem. Abstr.* 88 (1978) 198544p.

19. T. N. Srivastava, V. Kumar, and O. P. Srivastava, *Natl. Acad. Sci. Lett. (India)*, 1 (1978) 97; *Chem. Abstr.*, 89 (1978) 141068c.

20. J. P. Duchemin, M. Bonnet, and D. Huyghe, *Rev. Tech. Thomson-CSF*, 9 (1977) 685; *Chem. Abstr.*, 89 (1978) 14874n.

21.  A. L. Lin, V. Dao, and L. F. Donaghey, *Proc. Electrochem. Soc.*, 77 (1977)
     (Proc. Intl. Conf. Chem. Vap. Deposition, 6th) 264; *Chem. Abstr.*, 89 (1978)
     51545b.

22.  L. S. Ivanov, B. P. Baronenkova, N. P. Fatyushina, V. M. Timashkov, N. G.
     Lenivova, and V. N. Karpukhin, *Nauch. Tr. N.-i. i Proekt. In-t Redkomet.
     Prom-sti*, (1978) 42; *Chem. Abstr.*, 90 (1979) 47376a.