

GALLIUM AND INDIUM

ANNUAL SURVEY COVERING THE YEAR 1973

Rokuro Okawara

Department of Applied Chemistry, Osaka University, Yamadakami,
Suita, Osaka (Japan)

The study of gallium and indium derivatives has remained at about the same level during 1973 as during 1972 with a modest amount of structural and spectroscopic work, studies on synthesis and reaction chemistry, and applications. This survey will deal with these topics in this order. A review on "Organometallic eight-membered ring compounds of the elements Al, Ga, In, and Tl" with 125 references has been published (1).

Structural and Spectroscopic Studies

The crystal structures, as determined by diffraction method, of alkali metal tetramethyl indates, $M\text{In}(\text{CH}_3)_4$ ($M = \text{K}, \text{Rb}, \text{Cs}$) have been reported (2). The results showed that all the compounds consist of isolated alkali cations and tetrahedral $\text{In}(\text{CH}_3)_4$ anions, with In-C distances of 2.239(3) Å in $\text{KIn}(\text{CH}_3)_4$ and 2.26(2) Å in $\text{CsIn}(\text{CH}_3)_4$. The same authors reported (3) on the structures of alkali metal tetraphenylindates, $M[\text{In}(\text{C}_6\text{H}_5)_4]$. These were prepared by reaction of the alkali metal and triphenylindium in diethyl ether.

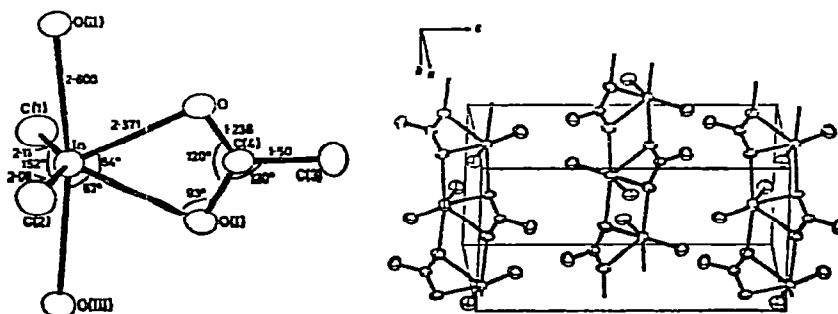


($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$)

These indates are colorless crystalline powders and are extremely sensitive to air and water. In all the compounds the presence of the $\text{In}(\text{C}_6\text{H}_5)_4$ anion was suggested by their IR spectra. The results of a crystal structure determination of $\text{NaIn}(\text{C}_6\text{H}_5)_4$ from the single crystal data showed that the compound consists of tetrahedral $\text{In}(\text{C}_6\text{H}_5)_4$ anions and Na cations ($\text{In}-\text{C}$, 2.230(3) Å), and that it is isostructural with $\text{LiIn}(\text{C}_6\text{H}_5)_4$.

The structures of dimethylindium acetate, $(\text{CH}_3)_2\text{InOOCCH}_3$ and diethylindium acetate, $(\text{C}_2\text{H}_5)_2\text{InOOCCH}_3$ have been studied by two groups (4,5). The methyl and ethyl compounds are white crystalline solids that can be sublimed in high vacuum. They are sparingly soluble in organic solvents. They are soluble in oxygen-free cold water and these solutions are stable for a short time. In the solution of the methyl compound, the presence of $\text{In}(\text{CH}_3)_2^+$ and CH_3COO^- was suggested by IR, Raman and molecular weight determinations. However, in the solid the presence of non-linear InC_2 and covalent InO was suggested by spectroscopic studies.

The structures of the methyl compound (4) and the ethyl analog (5) have been established by X-ray crystallographic studies. The results obtained for $(\text{CH}_3)_2\text{InOOCCH}_3$ are shown below.

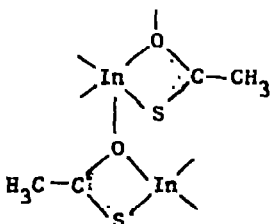


Figures 1 and 2. Structure of $(\text{CH}_3)_2\text{InOOCCH}_3$.

The structure of the ethyl analog is very similar to that of the methyl

compound. The only major difference that is obvious between the ethyl and methyl structure (see Fig. 1) is that the In-C (2.22, 2.29 Å) and In-O (2.44, 2.67 Å) bond lengths of the ethyl analog all appear to be longer and that the C-In-C angle (125.7°) is much smaller. From Figs. 1 and 2, it is understandable that each indium atom is six-coordinated and forms a planar four membered ring with the acetate group. The In-O distance within such a ring is only a little shorter than the distance of this oxygen to the indium of the next neighboring ring.

Dialkylindium thioacetates, $R_2\text{InOSCCH}_3$ ($R = \text{CH}_3, \text{C}_2\text{H}_5$) also were studied (6) by IR and Raman spectroscopy and the structure of the ethyl compound was established by an X-ray crystallographic study. The results showed that the thioacetate group is chelated to the indium atom to form a four membered ring, similar to the case of dimethyl- or diethylindium acetate described above. However, the sulfur atom in the four membered ring does not coordinate further to the other indium atom. Thus the indium atom is five coordinated, as shown schematically below.



The In-O distance within the four membered ring (2.582 Å) is nearly the same as the distance between the oxygen and the indium atom of the adjacent ring (2.450 Å).

The crystal structure of a dideuterio(pyrazol-1-yl)gallane dimer, $[\text{C}_3\text{H}_3\text{N}_2 \cdot \text{GaD}_2]_2$ has been investigated (7). The general view of the molecule, showing the symmetrical six-membered Ga(N-N)₂Ga ring in the boat form, is shown in Fig. 3.

The ^{115}In NQR parameters and those for the Sb isotopes and ^{75}As , in the 1:1 complexes of $(\text{CH}_3)_3\text{In}$ with $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_3\text{As}$, and $(\text{CH}_3)_3\text{Sb}$ have been

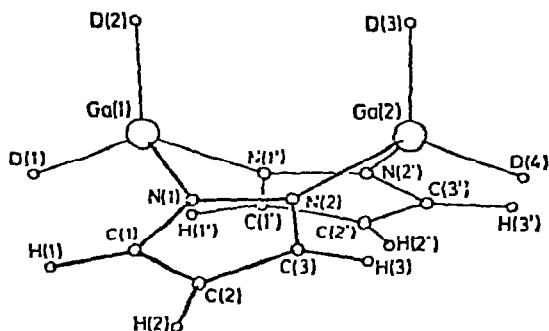


Figure 3 Molecular structure of $[\text{C}_3\text{H}_3\text{N}_2\cdot\text{GaD}_2]_2$

reported (8). These data are discussed in the light of those for the analogous series of $(\text{CH}_3)_3\text{Al}$ complexes, and the available thermodynamic data, and are concluded to be consistent with a small amount of (d-d) π bonding in the $(\text{CH}_3)_3\text{In}$ complexes with $(\text{CH}_3)_3\text{P}$ and its heavier congeners.

Magneto-optical rotation, magnetic susceptibility and the refractive index of chloroalkylgallium $\text{Cl}_n\text{R}_{3-n}\text{Ga}$ ($\text{R} = \text{C}_2\text{H}_5, \text{C}_4\text{H}_9$; $n = 0, 1, 2, 3$) have been measured (9). All these compounds are dimeric. The covalent character of the Ga-C and Ga-Cl bonds, as well as the coordination character of bridging Ga-Cl, were calculated.

Synthesis and Reactions

A convenient laboratory preparation of $\text{In}(\text{CH}_3)_3$ (75~95% yield, based on the charged In), from indium metal and dimethylmercury, has been described in detail (10), as was the direct preparation of trimethylgallium (yield, 70%) in ether from Mg and Ga powder by slow addition of CH_3I (11). Reactions of trimethylgallium with alkali metal hydrides were studied (11). With LiH in ether $(\text{CH}_3)_3\text{Ga}$ gave the complex $\text{Li}(\text{CH}_3)_3\text{GaH}$. Russian researchers also reported the preparation of R_3Ga ($\text{R} = \text{C}_{1-5}\text{alkyl}$) in 38-80% yield by heating alkyl halides with a Ga-Mg alloy at 100-150° in various solvents (12), the electrolytic formation of organogallium compounds (13) and the effect of trace elements (14) in the synthesis of $(\text{CH}_3)_3\text{Ga}$ from Ga, Mg and CH_3I , from GaCl_3 and CH_3MgI in $(\text{C}_2\text{H}_5)_2\text{O}$.

Pseudohalide complexes (15) of trialkylgallium(III) compounds have been prepared from R_3Ga and $[N(CH_3)_4]X$.

1/1 complex; $[N(CH_3)_4][R_3GaX]$ ($R = CH_3, C_2H_5$; $X = CN, NCO, NCS, N_3$)

2/1 complex; $[N(CH_3)_4][(R_3Ga)_2X]$ ($R = CH_3, C_2H_5$; $X = CN, N_3$).

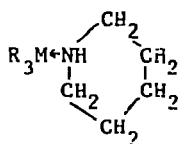
Occurrence of the following gallium-pseudohalide bonding can be deduced on the basis of IR and Raman spectral studies:

1/1 complex; $[R_3Ga-CN]^-$, $[R_3Ga-NCO]^-$ and $[R_3Ga-SCH]^-$

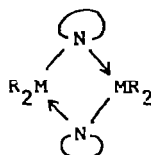
2/1 complex; $[R_3Ga-CN-GaR_3]^-$ and $[R_3Ga \backslash NNN]^-$.

Adducts with triethylarsine and triethylamine, $R_3Ga.M(C_2H_5)_3$ ($R = CH_3, C_2H_5$; $M = As, N$) and $(C_2H_5)_2GaCl.M(C_2H_5)_3$ have been prepared (16). Such adducts, in contrast to the uncomplexed gallium alkyls, are stable in air and can be distilled in vacuum.

Piperidine adducts, I, of R_3Ga ($R = CH_3, C_2H_5, i-C_4H_9$) or R_3In ($R = C_2H_5, i-C_4H_9$) have been prepared in n-pentane (17).



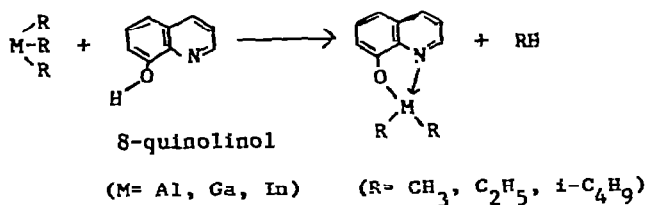
[I]



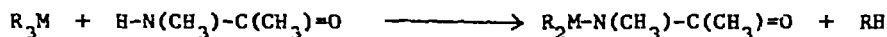
[II]

On heating the adducts at an appropriate temperature between 120° to 185° , dimeric compounds of the type II were obtained. From the analysis of IR and NMR data, the C-M bond polarity in those two types of compounds is discussed. A possible explanation is given by introducing a participation of the d-orbitals of the metal atom in the bonding. The preparation of monomeric complexes, R_2MQ ($Q =$ quinolin-8-olate) was described in detail by the same authors (18).

The reactivity of C-M bond of these yellow crystalline complexes is much reduced compared to that in the free metal alkyls. Mass spectra, ligand π -metal d (or s) transitions by electronic spectra and metal-nonmetal vibrations by IR spectra, were discussed.

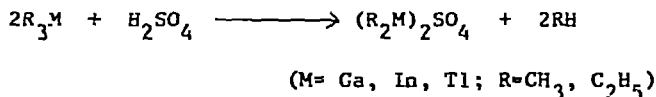


Dialkylgallium and indium derivatives of N-methylacetamides ($R_2M-N(CH_3)-C(CH_3)=O$; R= CH₃, C₂H₅; M= Ga, In) have been prepared (19) by a usual reaction in benzene.



The gallium compounds are dimeric in benzene. The indium compounds are sparingly soluble in organic solvents. A dimeric structure with a eight membered ring (see ref. 1) through OCN-bridges was discussed on the basis of the IR, and NMR data.

The reaction of trialkylgallium, -indium and -thallium with anhydrous sulfuric acid in a 2/1 molar ratio leads to dialkylmetal sulfates (20) of the composition $(R_2M)_2SO_4$.

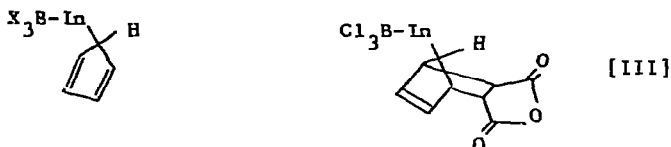


IR, Raman and NMR studies of these compounds were carried out. These compounds are dissociated in water into R_2M^+ and SO_4^{2-} ions. In the solid state, the SO_4^{2-} ion is distorted tetrahedral and the local symmetry of R_2Ga and $(CH_3)_2In$ is C_{2v} .

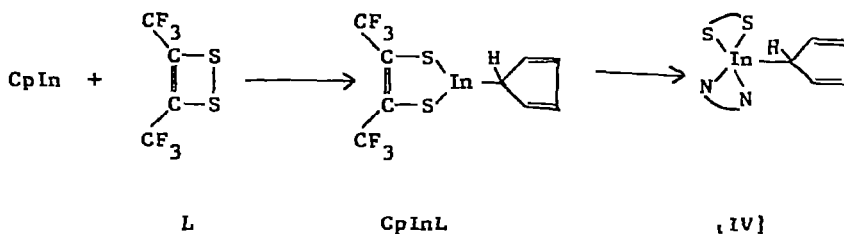
An interesting oxidative addition-type synthesis of $RInX_2$ (R= CH₃, C₂H₅, n-C₃H₇, n-C₄H₉; X= Br, I) from In(I) halides and organic halides, RX, has been reported (J. Organometal. Chem. 43 (1972) 257). The same authors (21) have extended this reaction to more reactive organic halides and isolated complexes of type $RInX_2$.dioxane (R= allyl, benzyl; X= Br, I):

Adducts of cyclopentadienylinidium(I), CpIn, and its oxidative addition

reactions have been reported. Cyclopentadienylindium in chloroform reacts with gaseous BX_3 ($X = F, Cl, Br, \text{ or } CH_3$) to yield solid $CpInBX_3$ (22). IR shows that the BX_3 group has the expected trigonal-pyramidal structure. The cyclopentadienyl ligand is in the monohapto(σ -bonded diene) form in the adduct. As in the case of $CpIn$ itself, this adduct reacts easily with maleic anhydride to give the product III.



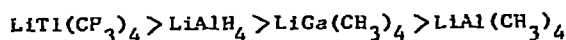
$CpIn$ reacts readily with 1,2-bis(trifluoromethyl)dithiete (L) to yield the solid compound $CpInL$ (23). $CpInL$ is thought to be polymerized in the solid owing to the coordinative unsaturation associated with formally three-coordinate indium(III). It is unstable in the presence of strong monodentate donors. However, stable monomeric, five-coordinate addition compounds, IV, were formed with 2,2'-bipyridine and 1,10-phenanthroline.



The cyclopentadienyl ligands in $CpInL$ and IV are believed to be of the σ -bonded diene form.

It has been reported (24) that the cleavage of the Sn-Sn bond in $(CH_3)_3SnSn(CH_3)_3$ in $CH_3OCH_2CH_2OCH_3$ by $LiMR_4$ ($M = Al, Ga, Tl; R = H, CH_3$) gives $(CH_3)_3SnR$. Neither $LiB(CH_3)_4$ nor $LiBH_4$ reacted with the ditin compound, even

after heating for 2 weeks at 80°. The overall rate of reactivity of LiMR_4 with the ditiin decreased as follows.



Applications and Patents

For the use of semiconductor materials, InAs , InP , $\text{Ga}_{1-x}\text{In}_x\text{As}$, and $\text{InAs}_{1-x}\text{P}_x$ have been prepared as single crystal films on Al_2O_3 and GaAs substrates by the chemical vapor deposition reactions of Et_3In and Me_3Ga with AsH_3 and PH_3 (25). For the system InAs-GaAs , the bandgap energy was determined as a function of composition.

Russian patents claimed that $(\text{CH}_3)_3\text{Ca}$ and $(\text{CH}_3)_3\text{In}$ can be prepared by heating CaX_3 and InX_3 ($\text{X} = \text{halogen}$) with $(\text{CH}_3)_3\text{Al-KCl}$ (26), and that the purity of the complexes obtained by reacting gallium alkyls with organic compounds of Group V or VI elements was increased by using alkyl gallium etherates (27).

REFERENCES

1. J. Weidlein, *J. Organometal. Chem.*, 49 (1973) 257.
2. K. Hoffmann and E. Weiss, *J. Organometal. Chem.*, 50 (1973) 17.
3. K. Hoffmann and Weiss, *J. Organometal. Chem.*, 50 (1973) 25.
4. F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, (1973) 248.
5. H. D. Hausen and H. U. Schwering, *Z. Anorg. Allg. Chem.*, 398 (1973) 119.
6. H. D. Hausen and H. J. Guder, *J. Organometal. Chem.*, 57 (1973) 243.
7. D. F. Rendle, A. Storr and J. Trotter, *J. Chem. Soc., Dalton Trans.*, (1973) 2252.
8. D. B. Patterson and A. Carnevale, *J. Chem. Phys.*, 59 (1973) 6464.
9. R. Haran and J. P. Laurent, *Bull. Soc. Chim. France*, (1973) 1673.
10. P. Krommes and J. Lorberth, *Inorg. Nucl. Chem. Lett.*, 9 (1973) 589.
11. V. V. Gavrilenko, N. P. Fatyushina, V. A. L'vova, V. S. Kolesov, Yu. N. Karaksin, and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1973) 126; *C. A.* 78 (1973) 136361m.

12. V. I. Bregadze, L. M. Golubinskaya, L. G. Tonoyan, B. I. Kozyrkin, and B. G. Gribov, Dokl. Akad. Nauk SSSR, 212 (1973) 880; C. A. 80 (1974) 48076h.
13. I. N. Chernykh and A. P. Tomilov, Elektrokhimiya, 9 (1973) 1025; C. A. 79 (1973) 99744w.
14. B. G. Gribov, B. I. Kozyrkin, V. A. Federov, V. A. Nikol'skii, and V. S. Solomatina, Dokl. Akad. Nauk SSSR, 208 (1973) 906 [Chem Technol]; C. A. 78 (1973) 148026u.
15. K. Dehnicke and Ian L. Wilson, J. Chem. Soc., Dalton Trans., 1428 (1973)
16. E. N. Zorina, B. G. Gribov, V. I. Kozyrkin, and E. B. Sokolov, Sb. Nauch. Tr. Probl. Mikroelektron., Mosk. Inst. Elektron, Tekh., 13 (1972) 90; C. A. 79 (1973) 146583v.
17. B. Sen and G. L. White, J. Inorg. Nucl. Chem., 35 (1973) 2207.
18. B. Sen and G. L. White, J. Inorg. Nucl. Chem., 35 (1973) 497.
19. H. U. Schwering and J. Weidlein, Chimia, 27 (1973) 535.
20. H. Olapinski and J. Weidlein, J. Organometal. Chem., 54 (1973) 87.
21. M. J. S. Gynane, L. G. Waterworth, and I. J. Worrall, Inorg. Nucl. Chem. Lett., 9 (1973) 543.
22. J. G. Conteras and D. G. Tuck, Inorg. Chem., 12 (1973) 2596.
23. A. F. Berniaz and D. G. Tuck, J. Organometal. Chem., 51 (1973) 113.
24. A. T. Weibel and J. P. Oliver, J. Organometal. Chem., 57 (1973) 313.
25. H. M. Manasevit and W. I. Simpson, J. Electrochem. Soc., 120 (1973) 135.
26. L. M. Golubinskaya, V. I. Bregadze, and O. Yu. Okhlobystin, U. S. S. R. 375, 293 (Cl. C07f); C. A. 79 (1973) 53528r.
27. B. G. Gribov, B. I. Kozyrkin, and E. N. Zorins, U. S. S. R. 371, 238 (Cl. C07f); C. A. 79 (1973) 53527q.