TABLE V

MOLECULAR WEIGHT CONCENTRATION DEPENDENCE OF 1:1 MOLAR MIXTURES OF $CoCl_2$ AND LiCl IN ACETONITRILE

10^2C,[a] *m*	Eff mol wt	10^2C,[a] *m*	Eff mol wt	10^2C,[a] *m*	Eff mol wt
1.00	91.0	4.00	102	7.00	104
2.00	97.5	5.00	103	8.00	104
3.00	101	6.00	104		

[a] Formal concentration of $CoCl_2$ which is equal to the formal concentration of LiCl.

TABLE VI

THEORETICAL MOLECULAR WEIGHTS FOR POSSIBLE SOLUTE INTERACTIONS IN THE $CoCl_2$–LiCl SYSTEM[a]

	Theoretical interaction	Eff mol wt
A.	$2CoCl_2 + 2Li^+ + 2Cl^- \rightleftarrows 2Li^+ + (CoCl_3^-)_2$	115
B.	$CoCl_2 + Li^+ + Cl^- \rightarrow$ no interaction	57
C.	$CoCl_2 + LiCl \rightarrow$ no interaction	86
D.	$2CoCl_2 + 2LiCl \rightleftarrows 2LiCl + (CoCl_2)_2$	115
E.	$2CoCl_2 + 2Li^+ + 2Cl^- \rightleftarrows 2Li^+ + 2Cl^- + (CoCl_2)_2$	69
F.	$CoCl_2 + Li^+ + Cl^- \rightleftarrows Li^+ + CoCl_3^-$	86

[a] In all equilibrium interactions, the theoretical molecular weight is based upon the assumption that the equilibrium is essentially displaced to the right.

the system would be expected to exhibit a theoretical effective molecular weight of 197 which would be essentially independent of the formal solution concentration. The results presented in Table III confirm this prediction and give further evidence that it is possible for $(CoCl_3^-)_2$ to exist in these acetonitrile solutions. It should be noted at this point that an apparent inconsistency exists in the concentration dependence of the effective molecular weight of 1:1 molar mixtures of Et_4NCl and $CoCl_2$ and the complex salt Et_4NCoCl_3. At the present time, no satisfactory explanation can be made adequately to account for this difference in the behavior of these two systems which should be chemically equivalent.

Absorption spectra of the Et_4NCoCl_3–CH_3CN system were determined and it was found that these complex salt solutions, like the 1:1 molar mixtures described above, exhibit spectra which are essentially identical with those generated in concentrated $CoCl_2$ solutions. This spectral identity lends even more support to the proposed dimerization process described by eq 6.

1:1 Molar Mixtures of $CoCl_2$ and LiCl.—A molecular weight and spectral study, similar to that carried out on 1:1 molar mixtures of $CoCl_2$ and Et_4NCl, was made on 1:1 molar mixtures of $CoCl_2$ and LiCl. The results of the molecular weight study are presented in Tables V and VI, and the absorption spectra of this system were found to be essentially identical with those presented in Figure 3 for 1:1 molar mixtures of $CoCl_2$ and Et_4NCl. By an interpretation analogous to that of the $CoCl_2$–Et_4NCl system, it can be concluded that similar interactions take place in the system composed of $CoCl_2$ and LiCl and that the formation of the ionic dimer $(CoCl_3^-)_2$ is not significantly affected by the size of the cation corresponding to the added chloride salt.

In conclusion, we wish to point out that while the data presented in this paper are consistent with the model described by eq 6, the absolute identification of complex ionic species in solution remains a very difficult task. Consequently, we cannot absolutely rule out certain other possibilities that might also be consistent with the data presented here.

CONTRIBUTION FROM THE CHEMICAL LABORATORIES,
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Double Isopropoxides of Aluminum, Gallium, and Indium

BY ANITA MEHROTRA AND R. C. MEHROTRA*

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A number of double isopropoxides of aluminum, gallium, and indium with the general formula $M\{M'(i\text{-}PrO)_4\}_3$ have been prepared by the reactions of the anhydrous chloride of one metal with the required quantity of potassium aluminum (or gallium) tetraisopropoxide or by refluxing together the two isopropoxides. The products are volatile under reduced pressure and can be recrystallized unchanged; they show molecular weights corresponding to the formula weights in benzene. Ir and nmr spectra have been recorded; the latter have been particularly useful in elucidating the structures of these new products.

Introduction

The pioneering work of Meerwein and Bersin[1] on double alkoxides appears to indicate that the combinations of strongly basic and acidic alkoxides generally tend to give stable "double alkoxo salts." The stability of a number of double alkoxides of lanthanide elements (La, Pr,[2] Nd, Sm, Dy, Yb, Y[3]) with aluminum and gallium recently synthesized in these laboratories is understandable from the above point of view. It has, therefore, been considered worthwhile to investigate whether the weakly basic elements aluminum, gallium, and indium tend to form double alkoxy species among themselves also.

Results

The synthesis of double isopropoxides of indium with aluminum and gallium has been carried out by reaction of anhydrous indium chloride with potassium, aluminum, or gallium tetraisopropoxide in 1:3 ratio in isopropyl alcohol

$$InCl_3 + 3KM(i\text{-}PrO)_4 \longrightarrow In\{M(i\text{-}PrO)_4\}_3 + 3KCl$$
$$M = \text{Al or Ga}$$

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(1) H. Meerwein and T. Bersin, *Justus Liebigs Ann. Chem.*, **476**, 113 (1929); *Chem. Abstr.*, **24**, 586 (1930).

(2) R. C. Mehrotra and M. M. Agarwal, *Chem. Commun.*, 469 (1968).

(3) M. M. Agarwal, Ph.D. Thesis, University of Rajasthan, Jaipur, 1968.

The potassium chloride formed in the above reaction immediately precipitates. After refluxing the reaction mixture for some time to ensure completion of the reaction, it is filtered. On concentration of the filtrate by removal of the solvent, a white solid crystallizes from the solution. The product corresponds in analysis to $\mathrm{In\{M(\textit{i}\text{-}PrO)_4\}_3}$ and can be recrystallized unchanged from anhydrous isopropyl alcohol. The molecular weights determined ebullioscopically in benzene also appear to correspond to the empirical formula $\mathrm{In\{M(\textit{i}\text{-}PrO)_4\}_3}$.

On heating the products under reduced pressure, $\mathrm{In\{Al(OPr\text{-}\textit{i})_4\}_3}$ and $\mathrm{In\{Ga(\textit{i}\text{-}PrO)_4\}_3}$ distil at 160° (0.3 mm) and 120° (0.1 mm), respectively. The distilled derivatives are silvery gray viscous liquids, solidifying slowly. Both are readily soluble in benzene.

The reaction between anhydrous indium chloride and potassium aluminum isopropoxide has also been attempted in 1:2 molar ratio when a white thick elastic type of material corresponding in analysis to $\mathrm{ClIn\{Al(\textit{i}\text{-}PrO)_4\}_2}$ is obtained. On heating the product under reduced pressure, it appears to disproportionate producing mainly volatile aluminum isopropoxide.

The indium–aluminum product has also been synthesized by refluxing the isopropoxides of the two elements in 1:3 and 1:>3 molar ratios in isopropyl alcohol

$$\mathrm{In(\textit{i}\text{-}PrO)_3 + 3Al(\textit{i}\text{-}PrO)_3 \longrightarrow In\{Al(\textit{i}\text{-}PrO)_4\}_3}$$

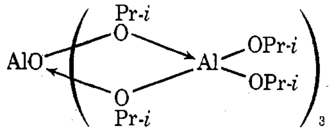
The products obtained in both cases were subjected to distillation under reduced pressure. In the latter case, excess aluminum isopropoxide distils out initially and products corresponding in analysis to $\mathrm{In\{Al(\textit{i}\text{-}PrO)_4\}_3}$ distil finally in both cases. The products obtained in this manner are identical in all their properties with the product obtained above in the reaction between indium chloride and potassium aluminum isopropoxide and correspond to the empirical formula $\mathrm{In\{Al(\textit{i}\text{-}PrO)_4\}_3}$.

Double isopropoxides of gallium and aluminum, corresponding in analysis to $\mathrm{Ga\{Al(\textit{i}\text{-}PrO)_4\}_3}$ and $\mathrm{Al\{Ga(\textit{i}\text{-}PrO)_4\}_3}$, have also been obtained by refluxing the isopropoxides of gallium and aluminum in 1:3 and 3:1 molar ratios, respectively, in isopropyl alcohol. The products can be recrystallized unchanged from isopropyl alcohol and show molecular weights corresponding to their formula weights in refluxing benzene.

Both products on being heated under reduced pressure distil unchanged in their composition at about 100–105° (0.5 mm) and 105–110° (0.2 mm), respectively.

Discussion

Structure of the Double Isopropoxides.—The volatility (*cf.* indium isopropoxide which is nonvolatile under the conditions), the unchanged analysis on repeated recrystallization, and the observed molecular weights of the double isopropoxides appear to confirm their identity. The ir spectra also have been recorded, but these do not give much additional evidence in this direction.



I

TABLE I

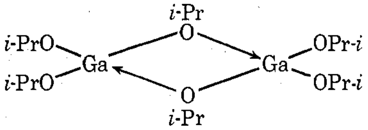
METHYL PROTON PEAKS IN PMR SPECTRA OF A FEW ISOPROPOXIDES (CPS) AT 60 MHz FROM TETRAMETHYLSILANE AT ROOM TEMPERATURE

Structure	Solvent	A	B	C	D	E	F	G	H
$\mathrm{Al(\textit{i}\text{-}PrO)_3}$	$\mathrm{CCl_4}$	91	85	80	74	69	63		
	$\mathrm{CDCl_3}$	93	87	82	76	71	65		
$\mathrm{[In\{Al(\textit{i}\text{-}PrO)_4\}_3]}$	$\mathrm{CCl_4}$	91	85	81	75	69	63		
(distilled)	$\mathrm{CDCl_3}$	91	85	81	75	69	63		
(recrystallized)	$\mathrm{CDCl_3}$	92	86	82	76	70	64		
$\mathrm{Ga(\textit{i}\text{-}PrO)_3}$	$\mathrm{CDCl_3}$	91	85	79[a]	73[a]	73	67		
$\mathrm{[In\{Ga(\textit{i}\text{-}PrO)_4\}_3]}$	$\mathrm{CDCl_3}$	91	85	83	77	73	67		
$\mathrm{Ga(\textit{i}\text{-}PrO)_3\cdot}$	$\mathrm{CCl_4}$	89	83	78	(72)	70	64	68	62
$\mathrm{3Al(\textit{i}\text{-}PrO)_3}$	$\mathrm{CDCl_3}$	94	88	83	77	75	69	73	67
$\mathrm{Al(\textit{i}\text{-}PrO)_3\cdot}$	$\mathrm{CCl_4}$	90	84	77	(71)	69	63	67	61
$\mathrm{3Ga(\textit{i}\text{-}PrO)_3}$	$\mathrm{CDCl_3}$	93	87	82	(76)	75	69	73	69

[a] In the spectrum of gallium isopropoxide, the doublet (79, 73) appears to grow on allowing the solution to stand, while the other two doublets gradually diminish in size.

The pmr spectra have, however, proved to be of great interest. Tetrameric aluminum isopropoxide has been assigned[4] structure I, in which the central aluminum atom is hexacoordinate and the three terminal aluminum atoms are tetracoordinate. The pmr spectrum of this derivative was first recorded by Shiner, *et al.*,[5] in 1963, and their conclusions have been recently confirmed by the work of Worrall and Oliver[6] as well as by the spectra presented in Table I. The spectrum of $\mathrm{\{Al(\textit{i}\text{-}PrO)_3\}_4}$ depicts essentially three types of methyl doublets; the high-field doublet is assigned to the six terminal isopropoxy groups, whereas the six bridging isopropoxy groups give rise to two almost equal doublets. The splitting of these low-field doublets has been ascribed by Shiner and coworkers to steric factors, whereas Worrall and coworkers[6,7] ascribe it to the asymmetry of the bridging oxygen.

The pmr spectrum[8] of a fresh solution of gallium isopropoxide in benzene has also been found to be similar to the above, indicating a structure of type I. However, on standing only one of the doublets increased in intensity while the other two became gradually insignificant. This has been explained by Oliver and Worrall[8] to be due to the dissociation of the tetrameric molecules on standing in solution to the following dimeric form, in which there appears to be a rapid interchange of terminal and bridging isopropoxy groups. Structure II for gallium isopropoxide appears to be stabilized by the tendency of gallium to attain preferably a four-coordination state.[8]



II

The peaks obtained in the 60-MHz spectra of the double isopropoxides prepared during the course of the

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[4] R. C. Mehrotra, *J. Indian Chem. Soc.*, **30**, 585 (1953); D. C. Bradley, *Advan. Chem. Ser.*, **No. 23**, 10 (1959).

[5] V. J. Shiner, Jr., D. Whittaker, and V. P. Fernandez, *J. Amer. Chem. Soc.*, **85**, 2318 (1963).

[6] J. G. Oliver and I. J. Worrall, *J. Chem. Soc.*, 845 (1970).

[7] T. N. Huckerby, J. G. Oliver, and I. J. Worrall, *Chem. Commun.*, 918 (1968); J. G. Oliver, P. K. Philips, and I. J. Worrall, *J. Inorg. Nucl. Chem.*, **31**, 1609 (1969).

[8] J. G. Oliver and I. J. Worrall, *J. Chem. Soc.*, 1389 (1970).

TABLE II

CHARACTERISTIC IR ABSORPTION BANDS OF $In(i\text{-}PrO)_3$, $Al(i\text{-}PrO)_3$, $Ga(i\text{-}PrO)_3$, $[In\{Al(i\text{-}PrO)_4\}_3]$, $[In\{Ga(i\text{-}PrO)_4\}_3]$, AND $[Ga\{Al(i\text{-}PrO)_4\}_3]$

$In(i\text{-}PrO)_3$	$Al(i\text{-}PrO)_3$	$Ga(i\text{-}PrO)_3$	$[In\text{-}\{Al(i\text{-}PrO)_4\}_3]$	$[In\{Ga(i\text{-}PrO)_4\}_3]$	$[Ga\text{-}\{Al(i\text{-}PrO)_4\}_3]$	Tentative assignment[9-11]
1375 s	1376 m	1370 s				
			1360 s	1360 s	1360 s	*gem*-Dimethyl
		1355 sh		1330 w		
			1216 s		1206 m	
1183 vs	1186 vs		1185 vs	1182 vs	1185 vs	Terminal ν(C–O + *i*-PrO)
1165 m	1171 vs	1165 s	1160	1166 m	1171 vs	OPr-*i*
1136 vs	1136 vs	1120 s, br	1140 s	1136 vs	1136 vs	Bridged ν(C–O + *i*-PrO)
			1125 vs	1120 vs	1121 vs	
1020 vw	1034 vs	995 s	1030 s	995 s	1034 s	Terminal ν(C–O)
965 s	946 vs	945 br	950 vs	944 vs	966 w	Bridged ν(C–O)
					948 vs	
	901 vs		855 w		856 w	
830 m	834 vs	845 m	830 m	840 w	834 s	
		740 s		820 m		
715 vw	696 s		695 w		696 m	ν(Al–O)
			665 m		671 m	ν(Ga–O)
		645 s		640 m		
580 m	573 m	595 s, br	586 w	590 m		
					558 w	
					540 w	
		535 br			530 w	
	474 w	485 m, br		470 w	470 w	

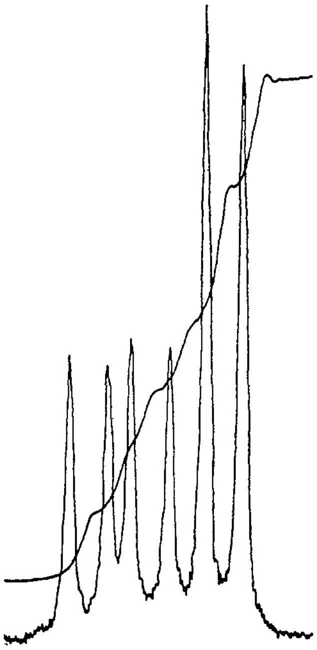
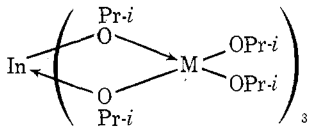


Figure 1.—The pmr spectra of methyl group protons of indium aluminum isopropoxide in $CDCl_3$.

present investigations are summarized in Table I. For comparison the data for the pmr spectra of aluminum and gallium isopropoxides, measured under the same conditions, have also been included. The spectrum of indium isopropoxide in $CDCl_3$ shows three ill-defined doublets of almost equal areas at δ 86, 80; 76, 70; and 72, 66, which remain almost unaltered even after 24 hr of standing in solution (see Figure 1). Characteristic ir absorption bands are shown in Table II.

In the spectra of $In\{Al(i\text{-}PrO)_4\}_3$ and $In\{Ga(i\text{-}PrO)_4\}_3$, the area of the doublets (E + F) is almost equal to the total area of the two doublets (A + B) + (C + D), which are almost equal in area between themselves. These spectra are thus almost identical with those of tetrameric aluminum isopropoxide and are consistent with a structure of the following type for the two double indium isopropoxides.



M = Al or Ga

A perusal of the covalent radii of In, Ga, and Al, as 1.44, 1.26, and 1.18 Å, respectively, shows that the radius of indium is so much larger that no appreciable interchange appears to occur between the central indium and terminal aluminum (or even gallium) atoms. This type of interchange does appear to take place in the double isopropoxides of aluminum and gallium. In the spectra of $Ga(i\text{-}PrO)_3 \cdot 3Al(i\text{-}PrO)_3$ as well as that of $Al(i\text{-}PrO)_3 \cdot 3Ga(i\text{-}PrO)_3$, the area of the doublets (A + B) + (C + D) is almost equal to that of the doublets (E + F) + (G + H). Further in all these spectra, the area of (A + B) is almost equal to that of (C + D). However, in the spectra of $Ga(i\text{-}PrO)_3 \cdot 3Al(i\text{-}PrO)_3$, the area of (G + H) is almost double that of (E + F), whereas in the spectrum of $Al(i\text{-}PrO)_3 \cdot 3Ga(i\text{-}PrO)_3$, the area of (G + H) is less than half that of (E + F). From a study of the position of terminal isopropoxy methyl protons in aluminum and gallium isopropoxides, the doublets (G + H) and (E + F) can be ascribed to the terminal isopropoxy groups attached to aluminum and gallium, respectively. This appears to indicate that interchange occurs between gallium and aluminum atoms and the above two double isopropoxides can be assigned the following structures mainly on the basis of their pmr spectra.

In the former case, structure III may be helped by the

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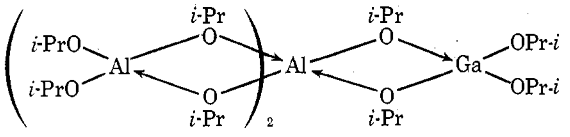
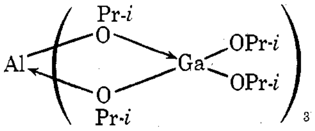
(9) C. T. Lynch, K. S. Mazdiyasni, J. S. Smith, and W. J. Crawford, *Anal. Chem.*, **36**, 2332 (1964).

(10) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, 2601 (1961).

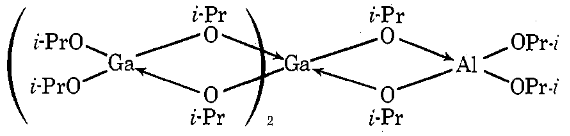
(11) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963.



III



IVa



IVb

greater stability of four-coordinate gallium, which also is indicated, as discussed above, by the pmr spectrum of gallium isopropoxide. In the latter case, structure IVb may be preferred due to larger radius of gallium but is not able to become the only species due to the preference of gallium for the four-coordination state and, hence, this derivative appears to be an equilibrium mixture of IVa and IVb.

Experimental Section

Apparatus.—All-glass apparatus with standard quickfit joints were used throughout. Extreme precautions were taken to exclude moisture.

Materials.—Indium chloride (Research Organic/Inorganic Chemical Corporation) and gallium chloride (Dr. Theodor Schuchardt) were used as such. Aluminum isopropoxide, obtained from N.C.L., Poona was distilled before use. Benzene (BDH) was dried initially on sodium and then azeotropically with ethanol and was finally collected at 80°. Isopropyl alcohol (BDH) was dried on sodium and aluminum isopropoxide and fractionated carefully before use.

Analysis.—The isopropoxy group was estimated by the usual technique of oxidation of potassium dichromate.[12] The estimation of indium, aluminum, and gallium in the compound was carried out as mixed metal oxides (denoted by *) or mixed metal oxinates (denoted by †); the analyses are marked as indicated according to the method employed. The chlorine content was estimated as silver chloride.

Molecular Weights.—A semimicro Gallenkamp ebulliometer with thermistor sensing was used for molecular weight determinations.

Nmr and Ir Spectra.—The nmr spectra were recorded with a Varian A-60 nuclear magnetic resonance spectrophotometer using anhydrous carbon tetrachloride and deuterated chloroform as solvents. Infrared spectra were recorded on a Perkin-Elmer Infracord 337.

Preparation of Indium and Gallium Isopropoxides.—Indium isopropoxide was prepared by treating the anhydrous indium chloride with potassium isopropoxide in a 1:3 molar ratio in isopropyl alcohol. The solution was refluxed for 2 to 3 hr and the precipitate of potassium chloride filtered off. Indium isopropoxide crystallized out in the filtrate after concentration of the solution. *Anal.* Calcd for $\mathrm{In}(i\text{-PrO})_3$: In, 39.3; *i*-PrO, 60.7. Found: In, 39.8; *i*-PrO, 59.9.

Gallium isopropoxide was prepared by the sodium method (bp 130° (0.3 mm)).[13] *Anal.* Calcd for $\mathrm{Ga}(i\text{-PrO})_3$: Ga, 28.2; *i*-PrO, 71.8. Found: Ga, 28.01; *i*-PrO, 71.2.

Reaction of Indium Chloride with Potassium Aluminum Isopropoxide in 1:3 Molar Ratio.—To a solution of anhydrous indium chloride (2.00 g) in ∽20 ml of isopropyl alcohol was added a solution of potassium aluminum isopropoxide, containing 1.11 g of potassium and 5.54 g of aluminum isopropoxide in ∽30 ml of isopropyl alcohol. An exothermic reaction occurred along with the immediate precipitation of potassium chloride. The reaction mixture was refluxed for about 2 hr. After allowing the potassium chloride precipitate to settle on cooling, the supernatant liquid was decanted out. White crystals appeared on concentrating the supernatant liquid by removal of the solvent. Analysis of the crystalline product obtained after drying corresponded to the formula $[\mathrm{In}\{(\mathrm{Al}(i\text{-PrO})_4\}_3]$. *Anal.* Calcd for $[\mathrm{In}\{\mathrm{Al}(i\text{-PrO})_4\}_3]$: (In + Al), 21.6; *i*-PrO, 78.4. Found: (In + Al), 22.2; *i*-PrO, 77.7.

The composition of the compound did not seem to vary on repeated recrystallization.

On subjecting the compound to distillation a silvery gray distillate was obtained at 160° (0.3 mm) in 60% yield. *Anal.* Calcd for $[\mathrm{In}\{\mathrm{Al}(i\text{-PrO})_4\}_3]$ as above, mol wt, 904: Found: (In + Al)*, 21.5; *i*-PrO, 78.2; mol. wt, (in benzene), 911.

$[\mathrm{In}\{\mathrm{Ga}(i\text{-PrO})_4\}_3]$ was prepared in a similar manner and the compound was recrystallized unchanged. *Anal.* Calcd for $[\mathrm{In}\{\mathrm{Ga}(i\text{-PrO})_4\}_3]$: (In + Ga), 31.4; *i*-PrO, 68.6. Found: (In + Ga)†, 31.4; *i*-PrO, 66.2.

The compound distilled as a silvery gray solid at 120° (0.1 mm) in 50% yield. *Anal.* Calcd for $[\mathrm{In}\{\mathrm{Ga}(i\text{-PrO})_4\}_3]$: as above; mol wt, 1033. Found: (In + Ga)†, 31.5; (In + Ga)*, 31.9; *i*-PrO, 68.1; mol wt (in benzene), 1153.

Reaction of Indium Isopropoxide With Aluminum Isopropoxide in 1:3 or 1:4 Molar Ratio.—Indium isopropoxide (3.08 g) and aluminum isopropoxide (6.49 g) in a 1:3 molar ratio were added to isopropyl alcohol (∽40 ml). The mixture was refluxed for about 2 hr. After cooling, the solvent was removed from the reaction mixture and the compound dried under reduced pressure and subjected to distillation. A silvery gray distillate was obtained at 158° (0.3 mm) in 50% yield. *Anal.* Calcd for $[\mathrm{In}\{\mathrm{Al}(i\text{-PrO})_4\}_3]$: (In + Al), 21.6; *i*-PrO, 78.4. Found: (In + Al), 21.5; *i*-PrO, 78.1.

Indium isopropoxide (2.01 g) was mixed with aluminum isopropoxide (5.62 g) in a 1:4 molar ratio in isopropyl alcohol (∽50 ml) and the solution was refluxed for 2 hr. The solid mass, obtained after removing the solvent, was subjected to distillation. A white viscous liquid corresponding in analysis to aluminum isopropoxide was initially obtained at 80° (0.5 mm) followed by a silver gray product at 162° (0.5 mm) which corresponds in analysis to $[\mathrm{In}\{\mathrm{Al}(i\text{-PrO})_4\}_3]$. *Anal.* Calcd for $\mathrm{Al}(i\text{-PrO})_3$: Al, 13.2; *i*-PrO, 86.8. Found (in white viscous liquid): Al, 13.1; *i*-PrO, 86.7. *Anal.* Calcd for $[\mathrm{In}\{\mathrm{Al}(i\text{-PrO})_4\}_3]$ as above. Found: (in silvery gray distillate): (In + Al), 22.0, *i*-PrO, 78.3.

Reaction of Gallium Isopropoxide and Aluminum Isopropoxide in 1:3 and 3:1 Molar Ratio.—For preparation of mixed gallium aluminum isopropoxides, mixtures of the two isopropoxides in molar ratios of 1:3 (gallium isopropoxide, 1.45 g; aluminum isopropoxide, 3.62 g) and 3:1 (gallium isopropoxide, 2.91 g; aluminum isopropoxide, 0.80 g), respectively, were refluxed separately in isopropyl alcohol. The solids obtained after removing the solvent in the two cases were subjected to distillation. The former distils at 100–105° (0.5 mm) and the latter at 105–110° (0.2 mm) and give analyses corresponding to the formulas $\mathrm{Ga}\{\mathrm{Al}(i\text{-PrO})_4\}_3$ and $\mathrm{Al}\{\mathrm{Ga}(i\text{-PrO})_4\}_3$.

Anal. Calcd for $\mathrm{Ga}\{\mathrm{Al}(i\text{-PrO})_4\}_3$: (Ga + Al), 17.5; Ga, 8.1; Al, 9.4; *i*-PrO, 82.5; mol wt, 860. Found: (Ga + Al)*, 17.6; (Ga + Al)†, 17.2; Ga, 8.2; Al, 9.2; *i*-PrO, 82.0; mol wt (in benzene), 829.

Anal. Calcd for $\mathrm{Al}\{\mathrm{Ga}(i\text{-PrO})_4\}_3$: (Al + Ga), 24.9; Al, 2.9; Ga, 22.1; *i*-PrO, 75.0; mol wt, 945. Found: (Al + Ga)*, 25.0; (Al + Ga)†, 25.2; Al, 3.0; Ga, 22.0; *i*-PrO, 75.8; mol wt, (in benzene), 950.

Reaction of Indium Chloride With Potassium Aluminum Isopropoxide in 1:2 Molar Ratio.—Anhydrous indium chloride (4.60 g) was dissolved in ∼20 ml of isopropyl alcohol. A solution, obtained by refluxing 1.67 g of potassium with 8.49 g of aluminum isopropoxide in ∼50 ml of isopropyl alcohol, was added to the indium chloride solution *via* a transfer tube. An exothermic reaction occurred along with the immediate precipitation of potassium chloride. The solution was then refluxed for ∼2 hr. The potassium chloride precipitate settled down on cooling and the supernatant liquid was decanted. The volatile solvent was distilled, and on subjecting the compound to final drying at 80° (0.9 mm) a white sticky substance was obtained and analyzed.

Anal. Calcd for $[\mathrm{ClIn}\{\mathrm{Al}(i\text{-PrO})_4\}_2]$: (In + Al), 35.5; *i*-PrO, 69.9; Cl, 5.3; mol wt, 676. Found: (In + Al), 34.9; *i*-PrO, 68.9; Cl, 5.3; mol wt (in benzene), 681.

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On subjecting the compound to distillation, a white viscous liquid with some silvery tinge was obtained at 128° (0.9 mm). The analysis of the distillate corresponded to that of aluminum isopropoxide. *Anal.* Calcd for $Al(i\text{-}PrO)_3$: Al, 13.2; *i*-PrO, 86.8. Found: Al, 13.2; *i*-PrO, 86.8.

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Metal Ions and Hydrogen Peroxide. XXVI.[1] On the Kinetics and Mechanism of the Catalase-Like Activity of Cobalt(III) Hematoporphyrin

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The disproportionation of H_2O_2, catalyzed by the Co(III) complex of hematoporphyrin IX ($Co^{III}HP$), was investigated in the pH range 5.5–10 by measuring the initial rate, v_0, of the increasing concentration of O_2 (25°, $I = 0.1$). In contrast to the usual inertness of Co(III) complexes the fifth and sixth coordination positions in $Co^{III}HP$ are sufficiently labile toward substitution to make $Co^{III}HP$ a usable catalyst. In the pH range 5.5–6.5 v_0 is proportional to $1/[H^+]$, in the pH range 8–10 v_0 is independent of the pH. At pH 6.15 v_0 is proportional to $[H_2O_2]^2$ and at pH 9.20 to $[H_2O_2]$. This is evidence that in the higher pH range 8–10 the catalyst is present as a peroxo complex, $CoHP(OOH^-)$. In the whole pH range v_0 is proportional to $[Co^{III}HP]$. Based on these experimental results the following reaction scheme was postulated

$$H_2O_2 \overset{K^{H}_{H_2O_2}}{\rightleftharpoons} H^+ + OOH^-$$

$$Co^{III}HP + OOH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co^{III}HP(OOH^-)$$

$$Co^{III}HP(OOH^-) + H_2O_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Co^{III}HP(OOH^-)H_2O_2$$

$$Co^{III}HP(OOH^-)H_2O_2 \xrightarrow{k_5} Co^{III}HP + H_2O + OH^- + O_2$$

By using the steady-state approximation a rate law was derived which is in accord with the above mechanism. From experiments with $[H_2O_2]_{tot(t=0)} > [Co^{III}HP]_{tot}$ the kinetic parameters were determined: $k_1 = 5.01 \times 10^6\ M^{-1}\ sec^{-1}$, $k_2 = 7.2 \times 10^{-2}\ sec^{-1}$, $(k_4 + k_5)/k_3 = 1.95 \times 10^{-3}\ M$, and $k_5 = 6.76 \times 10^{-2}\ sec^{-1}$. The stability constants of the peroxo adducts are $\log K^{CoHP}{}_{CoHP(OOH)} = 7.84$ and $\log K^{CoHP(OOH)}{}_{CoHP(OOH)(H_2O_2)} \geqslant 2.7$. From these results $\log v_0$ could be calculated with dependence on pH; the obtained curve is in excellent agreement with the experimental one. Hence, the postulated mechanism is in accord with all experimental facts. The structure of the active species is discussed; as the two peroxo ligands, OOH^- and H_2O_2, must be bound in a trans arrangement, it is suggested that the electron transfer occurs through the metal ion. In general $Co^{III}HP$ is significantly more active than is usual for Co(III) complexes. However, the catalase-like activity of $Co^{III}HP$ is of comparable order to the one due to other metal ion complexes.

The disproportionation of hydrogen peroxide in a homogenous phase is catalyzed by metal ions and their complexes. A suitable catalyst for reaction 1 has to

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \qquad (1)$$

have at least the following three distinct qualities. (i) The metal ion has to be redox active; *i.e.*, there must be two or more different oxidation states of reasonable stability.[2,3] (ii) "Free" coordination positions must be available, because the reaction proceeds within the coordination sphere of the metal ion; *i.e.*, H_2O_2 or derivatives thereof must be able to coordinate at the metal ion.[4] (iii) The coordination sphere of the metal ion must be "labile"; *i.e.*, sufficiently high exchange rates are necessary that a catalyst may be effective.

Among the metal ions with a pronounced catalase-like activity, iron(III) and copper(II) are probably most well known. Both metal ions fulfill the mentioned conditions i and iii; ii is easily achieved by selecting suitable ligands, *e.g.*, hematoporphyrin[5] or 4,4′,4′′,4′′′-tetrasulfophthalocyanine[6] with Fe^{3+}, or 2,2′-bipyridyl[7] with Cu^{2+}.

Due to the usual inert behavior of cobalt(III) complexes, these were so far not considered as very active catalysts. However, recently Fleischer, *et al.*,[8] have demonstrated that cobalt(III)–hematoporphyrin is rather labile with respect to substitution reactions. This report stimulated us to study the kinetics of the catalase-like activity of the Co(III) complex of hematoporphyrin IX,[9] which is indeed significantly more

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