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PREPARATION AND PROPERTIES OF ORGANOINDIUM COMPLEXES

TAKAYOSHI MAEDA and ROKURO OKAWARA
Department of Applied Chemistry, Osaka University, Suita, Osaka (Japan)
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SUMMARY

$(CH_3)_2InDtc$ [$Dtc=SSCN(CH_3)_2$], $RIn(Dtc)_2$, $(C_2H_5)_2InOx$ (Ox = Oxinate) and $R_2InOC_2H_4N(CH_3)_2$ were synthesized ($R=CH_3$ and C_2H_5). It is suggested that $(CH_3)_2InDtc$ and $RIn(Dtc)_2$ contain tetra- and pentacoordinate indium, respectively. R_2InOx is proposed to have a dimeric structure (I) with pentacoordinate indium. For $R_2InOC_2H_4N(CH_3)_2$, a dimeric structure (II) containing weak In–N coordination bonds is probable.

INTRODUCTION

Organoindium compounds are known to have a strong tendency to expand their coordination number to more than three[1], and in some instances air-stabilization is achieved by higher coordination[2].

To obtain air-stable organoindium compounds, we have prepared and investigated the properties of several new complexes containing potentially chelating ligands such as *N,N*-dimethyldithiocarbamate, oxinate and 2-(dimethylamino)-ethoxide.

EXPERIMENTAL

Starting materials

$(CH_3)_3In$[3], $(C_2H_5)_3In$[3], $(CH_3)_2InOAc$[4] and $(C_2H_5)_2InCl$[5] were prepared by the reported methods. $(C_2H_5)_2InOAc$ was prepared in a manner similar to $(CH_3)_2$-InOAc.

Preparations of $(CH_3)_2InSSCN(CH_3)_2$ and $CH_3In[SSCN(CH_3)_2]_2$

$(CH_3)_2InOAc$ (1.25 g, 6.13 mmole) in ice-cold water was added to an aqueous solution of $NaSSCN(CH_3)_2$ (1.0 g, 7.0 mmole). The white precipitate immediately formed was dried under vacuum to give 1.10 g of $(CH_3)_2InSSCN(CH_3)_2$ (68%).

$(CH_3)_2InSSCN(CH_3)_2$ (0.399 g, 1.51 mmole) in methanol (30 ml) was allowed to stand for a day. The pale yellow crystalline solid obtained was recrystallized from benzene to give $CH_3In[SSCN(CH_3)_2]_2$ (0.271 g, 48.5%).

Reaction of $(C_2H_5)_2InOAc$ with $NaSSCN(CH_3)_2$

$(C_2H_5)_2InOAc$ (2.46 g, 10.6 mmole) and $NaSSCN(CH_3)_2$ (2.5 g, 17.5 mmole) were reacted in a similar manner as above. The precipitate, which contained an appreciable amount of $C_2H_5In[SSCN(CH_3)_2]_2$, was purified by recrystallization from dichloromethane/petroleum ether to give only $C_2H_5In[SSCN(CH_3)_2]_2$ (0.93 g, 23 %). A similar result was obtained when $(C_2H_5)_2InCl$ was used as a starting material.

Preparation of $(C_2H_5)_2InOx$

$(C_2H_5)_2InOx$ was prepared in a manner similar to $(CH_3)_2InOx$[4]. IR spectra (Nujol mull): $\rho(In{-}CH_2)$, 633; $\nu(In{-}C)$, 506, 501 and 460 cm^{-1}. PMR spectra of oxinate protons (5 wt.%, TMS as an internal standard): 2-H, τ 2.03 (1.43); 4-H, τ 2.43 (1.71) in benzene (dichloromethane). UV spectra (3×10^{-4} *M*, in benzene at 25°): $(C_2H_5)_2InOx$, λ_{max} 370 nm (ε 3.4×10^3); $(CH_3)_2InOx$, λ_{max} 364 nm (ε 3.3×10^3).

Preparations of $R_2InOC_2H_4N(CH_3)_2$ *(*$R = CH_3$ *and* C_2H_5*)*

$HOC_2H_4N(CH_3)_2$ (3.00 g, 33.7 mmole) was added slowly to $(C_2H_5)_3In$ (6.60 g, 32.7 mmole) in hexane (40 ml) under an atmosphere of nitrogen. Evolution of ethane occurred, leaving a clear colourless solution. After removal of the solvent under reduced pressure, the residual solid was recrystallized from petroleum ether (8.29 g, 97 %). The reaction between $(CH_3)_3In$ and $HOC_2H_4N(CH_3)_2$ gave $(CH_3)_2InOC_2H_4N(CH_3)_2$ (95 %). IR spectra (Nujol mull): $(C_2H_5)_2InOC_2H_4N(CH_3)_2$, $\rho(In{-}CH_2)$, 625; $\nu(In{-}C)$, 485 and 453 cm^{-1}; $(CH_3)_2InOC_2H_4N(CH_3)_2$, $\rho(In{-}CH_3)$, 694; $\nu(In{-}C)$, 509 and 468 cm^{-1}.

Reactions of $R_2InOC_2H_4N(CH_3)_2$ *(*$R = CH_3$ *and* C_2H_5*) with* CH_3I

$(CH_3)_2InOC_2H_4N(CH_3)_2$ (2.20 g, 9.44 mmole) and CH_3I (6 ml) were mixed in benzene (15 ml) under an atmosphere of nitrogen and allowed to stand for four days at room temperature. The yield of precipitated $(CH_3)_2InOC_2H_4N(CH_3)_3I$ was 27.9 %. From the mother solution, 1.44 g (65.5 %) of $(CH_3)_2InOC_2H_4N(CH_3)_2$ was recovered. The reaction between $(C_2H_5)_2InOC_2H_4N(CH_3)_2$ and CH_3I was carried out similarly, the yield of $(C_2H_5)_2InOC_2H_4N(CH_3)_3I$ being about 19 % after four days. The amount of recovered $(C_2H_5)_2InOC_2H_4N(CH_3)_2$ was 1.61 g (77.5 %). $(C_2H_5)_2InOC_2H_4N(CH_3)_3I$ is highly sensitive to moisture. Crystallization of this compound from moist acetone gave $HOC_2H_4N(CH_3)_3I$. M.p. 259–260°. (Found: C, 26.17; H, 6.38; N, 6.07. $C_5H_{14}ONI$ calcd.: C, 25.99; H, 6.11; N, 6.06 %.)

The properties and analytical data of the organoindium compounds obtained are given in Table 1.

Physical measurements

Molecular weights in benzene solution were determined cryoscopically under an atmosphere of nitrogen, or by using a Mechrolab vapor pressure osmometer Model 302 at 25°. The UV spectra were measured on a Hitachi 124 spectrophotometer using a 1 cm cell. The IR spectra were obtained using a Hitachi Model 225 spectrophotometer equipped with gratings. The PMR spectra were recorded on a Japan Electron Optics JNM-3H-60 spectrometer.

RESULT AND DISCUSSION

$(CH_3)_2InDtc$ and $RIn(Dtc)_2$ *(*$R = CH_3$ *and* C_2H_5*)*

The compound $CH_3In(Dtc)_2$, which is fairly air-stable, was obtained from

TABLE 1

PROPERTIES OF SOME ORGANOINDIUM COMPOUNDS

Compound	*M.p.* (°C)	*Analysis found (calcd.) (%)*				*Mol.wt. (in benzene)*	
		C	*H*	*N*	*In*	*found*[a] (*calcd.*)	*Concn.* (*Wt. %*)
$(C_2H_5)_2InOAc$[b]	182–184	30.98 (31.06)	5.27 (5.65)		49.63 (49.49)	[c]	
$(CH_3)_2InSSCN(CH_3)_2$	120–125	22.54 (22.65)	4.59 (4.56)	4.90 (5.28)	43.56 (43.31)	260 (265)	1.24
$CH_3In[SSCN(CH_3)_2]_2$	206–208	22.74 (22.71)	4.10 (4.08)	7.67 (7.57)	30.61 (31.01)	361 (370)	2.00
$C_2H_5In[SSCN(CH_3)_2]_2$	117–121 (decomp.)	24.77 (25.00)	4.55 (4.46)	7.30 (7.29)	30.10 (29.88)	342 (384)	1.01
$(CH_3)_2InOx$[d,e]	>260	45.83 (45.71)	4.13 (4.18)	4.73 (4.85)	39.59 (39.72)	561[f] (289)	0.40
$(C_2H_5)_2InOx$[d]	222–229 (decomp.)	49.07 (49.24)	5.12 (5.09)	4.45 (4.42)	36.18 (36.21)	652[g] (317)	1.39
$(CH_3)_2InOC_2H_4N(CH_3)_2$	110–111	30.75 (30.93)	6.88 (6.92)	5.75 (6.01)	49.03 (49.27)	458 (233)	1.82
$(C_2H_5)_2InOC_2H_4N(CH_3)_2$	62–64.5	36.78 (36.81)	8.00 (7.72)	5.17 (5.37)	43.65 (43.98)	550 (261)	1.37
$(CH_3)_2InOC_2H_4N(CH_3)_3I$	218–221 (decomp.)	22.63 (22.42)	5.36 (5.11)	3.53 (3.73)	30.28 (30.62)	[c]	
$(C_2H_5)_2InOC_2H_4N(CH_3)_3I$	148–158 (decomp.)	[h]	[h]	[h]	28.25 (28.49)	[c]	

[a] Determined cryoscopically. [b] OAc=Acetate. [c] Not determined because of limited solubility. [d] Ox=Oxinate. [e] The known compound from ref. 4. [f] Determined by osmometry. [g] The values determined by osmometry are 563, 591, 619 and 635 at 0.24, 0.56, 1.06 and 2.06 wt. %, respectively. [h] Analysis was difficult because of its high sensitivity to moisture. See experimental section.

$(CH_3)_2InDtc$ in methanol in a yield of 48%. Although formation of $(CH_3)_3In$ was not confirmed, it is probable that the following disproportionation reaction had occurred.

$$2\,(CH_3)_2InDtc \rightarrow CH_3In(Dtc)_2 + [(CH_3)_3In]$$

$C_2H_5In(Dtc)_2$ was obtained from $(C_2H_5)_2InX$ (X=Cl and OAc) and NaDtc, and attempts to isolate the expected compound, $(C_2H_5)_2InDtc$, were unsuccessful.

All of the alkylindium *N,N*-dimethyldithiocarbamates shown in Table 1 were found to be monomeric in benzene. As shown in Table 2, the IR spectra of these compounds both in the solid state and in solution show ν(C–N) at about 1500 cm^{-1} and only one intense band associated with ν(C–S) in the region 1000±70 cm^{-1}. This observation indicates the existence of bidentate dithiocarbamate ligands[6] and shows that the indium atoms in $(CH_3)_2InDtc$ and $RIn(Dtc)_2$ are tetra- and pentacoordinate, respectively. The ν(In–C) frequencies in $(CH_3)_2InDtc$ are appreciably lower than those in $(CH_3)_2InAcac$ (542, 490 cm^{-1})[7,8] or $(CH_3)_2InOCOCF_3$ (564, 518 and 497 cm^{-1})[7], which have been reported to be monomeric compounds with tetracoordinate indium. This suggests that the dithiocarbamate ligand is strongly chelated to the dimethylindium moiety.

TABLE 2

IR DATA OF SOME ORGANOINDIUM *N,N*-DIMETHYLDITHIOCARBAMATES (cm^{-1})

Compound		*ν(C=N)*	*ν(C–S)*	*ν(In–C)*	*ν(In–S)*
$(CH_3)_2InSSCN(CH_3)_2$	Solid[a]	1515	965	521 485	373
	Solution[b]	1496	979	518 482	379
$CH_3In[SSCN(CH_3)_2]_2$	Solid[a]	1515	979	505	377
	Solution[c]	1490	982	506	379
$C_2H_5In[SSCN(CH_3)_2]_2$	Solid[a]	1510	976	487	377
	Solution[c]	1496	982	486	378

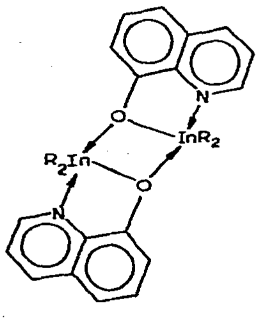
[a] Nujol and hexachlorobutadiene mulls. [b] In carbon tetrachloride (3 wt. %). [c] In chloroform (3 wt. %).

R_2InOx ($R=CH_3$ and C_2H_5)

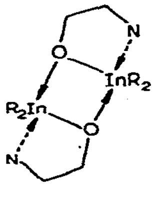
These compounds are stable in air and did not redistribute into $RIn(Ox)_2$ at room temperature. One of the characteristic features of these compounds is that they are dimeric in benzene (Table 1) in contrast with monomeric $(C_2H_5)_2GaOx$[9] and $(CH_3)_2TlOx$[*,10]. Their UV spectra in benzene (3×10^{-4} *M*) show an absorption band at 364 ($R=CH_3$) and 370 nm ($R=C_2H_5$) which falls in the region observed for a chelating oxinate ligand[12]. In the PMR spectra of $(C_2H_5)_2InOx$ (5 wt.%), the differences of the chemical shift in CH_2Cl_2 and C_6H_6, $[\delta(CH_2Cl_2)-\delta(C_6H_6)]$, of the 2- and 4-protons of the oxinate ligand were 0.60 and 0.72 ppm, respectively, which are similar to those of chelated organotin oxinates[13]. From the above results, a structure (I) with pentacoordinate indium seems to be most probable for R_2InOx. An analogous configuration has been known from the X-ray analysis of $[M(Ox)_2]_2$ ($M=Cu$[14] and Zn[15]) and $[(CH_3)_3PtOx]$[16].

$R_2InOC_2H_4N(CH_3)_2$ ($R=CH_3$ and C_2H_5)

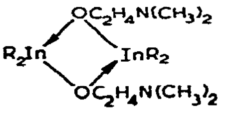
These compounds are dimeric in benzene (Table 1). They reacted rather slowly with CH_3I to give their quaternary ammonium salt $R_2InOC_2H_4N(CH_3)_3I$. The corresponding dimethylgallium compound has been reported[17] to react with CH_3I immediately and was proposed to have an uncoordinated nitrogen atom. Coordinated nitrogen is not reactive toward CH_3I as in the case of the analogous organozinc compounds[18,19]. Accordingly, for $R_2InOC_2H_4N(CH_3)_2$, a structure such as (II)



(I)



(II)



(III)

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[*] It has been reported[11] that $(CH_3)(C_2H_5)TlOx$ has a degree of association of 1.7.

containing weak In–N coordination bonds is more probable than a structure (III) which is similar to that of $(CH_3)_2GaOC_2H_4N(CH_3)_2$.

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