Synthesis of Tris(β-diketonato)indium from Metallic Indium and Bis(β-diketonato)copper

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Synopsis. The reaction between metallic indium and bis(β-diketonato)copper(II) in non-aqueous solution produced the corresponding indium chelate compounds of the type [In(dik)$_3$], where Hdik denotes $CH_3COCH_2COCH_3$ (Hacac), $CH_3COCH_2COC_6H_5$ (Hbzac), $C_6H_5COCH_2COC_6H_5$ (Hdbzm), or $(CH_3)_3CCOCH_2COC(CH_3)_3$ (Hdpm). The [In(acac)$_3$] was formed in high yield by the reactions using *o*-dichlorobenzene, decaline, or DMSO as solvent. The other indium chelate compounds were synthesized by reactions using DMSO as solvent.

Since the MOCVD (metal organic chemical vapor deposition) technique was developed, trialkyl indiums and metallo-organics of indium, such as indium chelates, acylates, and alkoxides have found practical applications. Among the indium compounds, the chelate compounds are much easier to handle than the other compounds. Tris(acetylacetonato)indium(III) was first prepared in 1921 by the reaction of acetylacetone (Hacac) with freshly prepared In(OH)$_3$.[1] The compound was obtained by the reaction of Hacac with an aqueous solution of indium chloride in the presence of tartaric acid and potassium hydroxide.[2] Tris(β-diketonato)indium(III) compounds have been also prepared by the reaction between an aqueous ethanolic solution (1 : 1) of a ligand and indium nitrate with aqueous ammonia at pH 4.[3] We have reported the synthesis of tris(β-diketonato)indium(III) and tris(β-ketoester)indium(III) by the reaction of anhydrous indium(III) chloride with β-diketones in the presence of amines or sodium cyanide in non-aqueous solution.[4] To isolate highly pure chelate compounds, it is important to use a pure In(OH)$_3$ and anhydrous indium(III) chloride as a starting material. However, it is not easy to control the reaction conditions for the preparation of the starting materials. Since metallic indium is unaffected by boiling water or alkali and does not form oxides readily in the air, its handling is very simple. Moreover, the first ionization potential of indium[5] is much lower than that of copper, i.e., In: 558.3 kJ mol^{-1} and Cu: 745.4 kJ mol^{-1}. So we have attempted the preparation of tris(β-diketonato)indium(III) by the reaction between metallic indium and bis(β-diketonato)copper(II) in non-aqueous solution. J. J. Habeeb and D. G. Tuck also reported the one-step synthesis of In(acac)$_3$ by a direct route involving the electrochemical oxidation of indium metal in a solution of Hacac in methanol.[6]

In this paper, we describe a simple method for preparing tris(β-diketonato)indium(III) by the following reactions using metallic indium:

$$\mathrm{In} + \mathrm{Cu(dik)_2} \xrightarrow{\text{org. solv.}} \mathrm{In(dik)_3} + \mathrm{Cu}$$

org. solv. : C_6H_5Cl, *o*-Cl-C_6H_4Cl, DMSO, or decaline.

dik : acac, bzac, dbzm, or dpm.

Results and Discussion

When the reaction between metallic indium and bis(acetylacetonato)copper(II) [Cu(acac)$_2$] was performed in acetonitrile, chloroform, tetrahydrofuran, or ethanol, a detectable amount of tris(acetylacetonato)indium(III) [In(acac)$_3$] was not formed (Entry 1-1—Entry 1-4 in Table 1), and the starting materials were recovered nearly quantitatively. The same results were also obtained by the reaction using chlorobenzene at 132 °C (Entry 1-5) or *N*,*N*-dimethylformamide (DMF) at 153 °C (Entry 1-6) as the solvent. These reactions were carried out at the temperatures below the melting point (156.6 °C) of metallic indium. In contrast, on heating the reaction mixture at 160 °C for 8 h in *o*-dichlorobenzene, DMSO, or decaline, [In(acac)$_3$] was formed in high yield without containing copper (Entries 1-7, 1-8, and 1-10). The yield of [In(acac)$_3$] was 83% in DMSO for 4 h (Entry 1-9). Characteristic absorption bands and the melting point of the isolated [In(acac)$_3$] are shown in Table 2. The results agree with those of the authentic sample obtained by the reaction of $InCl_3$ with Hacac in methanol in the presence of sodium cyanate.[4]

As shown in Entries 1-11, 1-12, and 1-13, similar reactions occurred between metallic indium and bis(benzoylacetonato)copper(II), Cu(bzac)$_2$, bis(dibenzoylmethanato)copper(II), Cu(dbzm)$_2$, or bis(pivaroylmethanato)copper(II), Cu(dpm)$_2$, at 160 °C in DMSO. The corresponding tris(β-diketonato)indium(III) complexes resulted in high yields. Whereas, similar reactions in *o*-dichlorobenzene afforded the corresponding tris(β-diketonato)indium(III) in 20—35% yield. The elemental analyses, melting points, and the characteristic absorption bands of IR spectra of the In(dik)$_3$ agree with those in the literature.[4,7] These results show that the reaction temperature plays a significant role in the reaction between metallic indium and bis(β-diketonato)copper(II) and that DMSO is an excellent solvent in the reaction using metallic indium.

Table 1. Reaction between In and $Cu(dik)_2$ in Various Solvents for 8 h

Entry	$Cu(dik)_2$ dik	Solvent	Temp °C	Products	Yield[a] %
1-1	acac	Tetrahydrofuran	61	—	—
1-2	acac	Chloroform	66	—	—
1-3	acac	Ethanol	78	—	—
1-4	acac	Acetonitrile	81	—	—
1-5	acac	Chlorobenzene	132	—	—
1-6	acac	DMF	153	—	—
1-7	acac	*o*-Dichlorobenzene	160	$In(acac)_3$	88
1-8	acac	Decaline	160	$In(acac)_3$	88
1-9	acac	DMSO	160	$In(acac)_3$	83[b]
1-10	acac	DMSO	160	$In(acac)_3$	85
1-11	bzac	DMSO	160	$In(bzac)_3$	83
1-12	dbzm	DMSO	160	$In(dbzm)_3$	81
1-13	dpm	DMSO	160	$In(dpm)_3$	81

a) Based on $Cu(dik)_2$. b) Reaction time: 4 h.

Table 2. Characterization Data of $In(dik)_3$

Entry	$In(dik)_3$	Anal./%[a] C	H	In	Mp °C	IR/cm^{-1} $\nu_{C=O}$	$\nu_{C=C}$	ν_{In-O}	
2-1	$In(acac)_3$	43.26 (43.71,	5.04 5.14,	27.7 27.86)	187	1582	1528	436	406
2-2	$In(bzac)_3$	59.92 (60.22,	4.44 4.55,	19.0 19.19)	212	1554	1516	422	406
2-3	$In(dbzm)_3$	68.64 (68.89,	4.22 4.24,	14.5 14.63)	253	1528		454	442
2-4	$In(dpm)_3$	60.09 (59.64,	8.59 8.64,	17.3 17.28)	172	1552	1508	500	576

a) Parenthesis indicates the calcd data for $In(dik)_3$.

Therefore, we think that the present synthetic method is a practical way to prepare tris(β-diketonato)indium(III) by using metallic indium, bis(β-diketonato)copper(II), and DMSO as solvent.

Experimental

All experiments were carried out in a nitrogen atmosphere passed through a tube which was immersed in liquid nitrogen.

Melting points were taken in capillary tubes and are uncorrected. The indium and copper content were determined by chelate titration with ethylenediaminetetraacetic acid in the In^{3+} oxidation state. IR spectra were recorded on a Hitachi IR 270-30 (4000—400 cm^{-1}) spectrometer as a suspension in Nujol. ^1H NMR spectra were measured with a Hitachi R-24B (60 MHz) spectrometer using TMS as an internal standard.

Bis(β-diketonato)coppers(II) were prepared by documented procedures[8] and commercial metallic indium was used without purification.

A typical compound of tris(β-diketonato)indium(III) was synthesized by the following procedure.

Metallic indium (2.3 g, 0.02 mol) and bis(acetylacetonato)copper(II) (3.93 g, 0.015 mol) were placed in *o*-dichlorobenzene (200 mL), and heated at 160 °C for 8 h with stirring. During the course of the reaction, the solution changed in color from dark purple to pale yellow, with the deposition of copper powders. After the mixture was dried under a reduced pressure, 30 mL of benzene and then 20 mL of hexane were added to the residue, and the insoluble matters were filtered off. The filtrate was evaporated to dryness and the residue was recrystallized in cyclohexane to give 3.6 g (88%) of $In(acac)_3$, mp 187 °C.

Similarly, all the other reactions were carried out and the products were recrystallized from dichloromethane–ethanol mixed solution (1 : 1). All the products obtained in this work are known compounds, so the structures were determined by the spectral data given in the literature.[4,7]

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