

Synthesis and Disproportionation of Mixed Ligand Indium Organometallics Involving Ethyl and β -Diketonate Chelate Ligands

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Twelve compounds either of type $\text{Et}_2\text{In}(\text{diket})$ or $\text{EtIn}(\text{diket})_2$ (diket = β -diketonate) have been synthesized, and all these compounds tend to disproportionate into Et_3In and $\text{In}(\text{diket})_3$ at moderately high temperature. Compounds of the latter type are much more thermally stable than those of the former. Moreover, $\text{In}(\text{CH}_3\text{COCHCOCH}_3)_3$ has been synthesized and its crystal structure has been determined.

Keywords Triethylindium, β -diketonate, disproportionation, organometallic compounds, structure

Introduction

Bangall¹ pointed out that the β -diketonate ligand in actinoid complexes is quite labile. We²⁻⁷ found that the lability of ligands is the cause of disproportionation reactions of lanthanoid organometallics involving cyclopentadienyl and other ligands. The purpose of this paper is to

extend the investigation of disproportionation reaction of indium complexes bearing ethyl and β -diketonate ligands.

Results and discussion

Adopting the very versatile method of liberating ethane from a $(\text{C}_2\text{H}_5)_3\text{In}$ moiety by the action of protonic acids stronger than C_2H_6 , we have synthesized thirteen compounds by the reaction of Et_3In with acetylacetone (H-acac), malonic ester ($\text{C}_2\text{H}_5\text{OCOCH}_2\text{COOC}_2\text{H}_5$, H-maes), acetylacetic ester ($\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$, H-acace), trifluoroacetylaceto acetyl- α -thiophene ($\text{SCH}=\text{CHCH}=\text{CCOCH}_2\text{COCF}_3$, H-tfacth), and benzoylacetone ($\text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3$, H-bzac), benzoyltrifluoroacetone ($\text{CF}_3\text{COCH}_2\text{COC}_6\text{H}_5$, H-bztfac). They are:

1:1 ratio of reactants		1:2 ratio of reactants		1:3 ratio of reactants	
$\text{Et}_2\text{In}(\text{acac})$	1	$\text{EtIn}(\text{acac})_2$	2	$\text{In}(\text{acac})_3$	13
$\text{Et}_2\text{In}(\text{maes})$	3	$\text{EtIn}(\text{maes})_2$	4		
$\text{Et}_2\text{In}(\text{acace})$	5	$\text{EtIn}(\text{acace})_2$	6		
$\text{Et}_2\text{In}(\text{tfacth})$	7	$\text{EtIn}(\text{tfacth})_2$	8		
$\text{Et}_2\text{In}(\text{bzac})$	9	$\text{EtIn}(\text{bzac})_2$	10		
$\text{Et}_2\text{In}(\text{bztfac})$	11	$\text{EtIn}(\text{bztfac})_2$	12		

1—12 are new compounds, all these compounds were characterized by elemental analysis IR (Table 1)

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and MS (Table 2) spectroscopy. In order to verify their bonding way between β -diketonate and In, the structure

of compound **13** was determined by single-crystal X-ray diffraction techniques.

Table 1 Analytical data for the compounds **1**—**13**

Compounds $\text{Et}_n\text{In}(\text{diket})_{3-n}$	Yield (%)	mp ($^{\circ}\text{C}$) (d = decomp.)	Colour	Analysis (Found(calcd.)(%))			IR 1500—1600 cm^{-1}
				In	H	C	
1	52	93—94	white	42.23 (42.28)	6.25 (6.25)	39.76 (39.71)	1515, 1561, 1590
2	61	110	white	33.66 (33.63)	5.54 (5.56)	42.14 (42.10)	1520, 1568, 1590
3	68	57—58	white	34.49 (34.46)	6.31 (6.33)	39.74 (39.76)	1527, 1562, 1578
4	45	95—96	white	24.86 (24.89)	5.77 (5.84)	41.59 (41.56)	1501, 1540, 1562
5	54	240(d)	pale yellow	37.74 (37.75)	6.28 (6.29)	39.91 (39.74)	1506, 1578, 1776
6	52	102(d)	white	28.64 (28.61)	5.70 (5.72)	41.72 (41.79)	1518, 1573, 1591
7	60	140(d)	orange red	29.15 (29.19)	3.54 (3.55)	36.53 (36.55)	1509, 1521, 1595
8	58	180	pale yellow	19.64 (19.62)	2.21 (2.22)	36.78 (36.86)	1541, 1565, 1585
9	53	75	pale yellow	34.39 (34.43)	5.66 (5.69)	50.24 (50.30)	1511, 1544, 1592
10	56	113—114	pale yellow	24.73 (24.68)	4.90 (4.94)	56.69 (56.65)	1548, 1587, 1597
11	62	53	pale yellow	29.72 (29.64)	4.09 (4.12)	43.19 (43.30)	1545, 1571, 1596
12	67	131	pale yellow	19.98 (20.03)	2.93 (2.96)	46.02 (46.00)	1533, 1566, 1592
13	80	187	colorless	27.85 (27.86)	5.01 (5.02)	43.73 (43.71)	1548, 1576, 1596

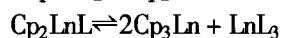
diket = $\text{CH}_3\text{COCHCOCH}_3$, $n = 2$ (**1**); diket = $\text{CH}_3\text{COCHCOCH}_3$, $n = 1$ (**2**); diket = $\text{C}_3\text{H}_5\text{OCOCHCOOC}_2\text{H}_5$, $n = 2$ (**3**);
diket = $\text{C}_2\text{H}_5\text{OCOCHCOOC}_2\text{H}_5$, $n = 1$ (**4**); diket = $\text{CH}_3\text{COCHCOOC}_2\text{H}_5$, $n = 2$ (**5**); diket = $\text{CH}_3\text{COCHCOOC}_2\text{H}_5$, $n = 1$ (**6**);
diket = $\text{SCH}=\text{CHCH}=\text{CCOCHCOCF}_3$, $n = 2$ (**7**); diket = $\text{SCH}=\text{CHCH}=\text{CCOCHCOCF}_3$, $n = 1$ (**8**);
diket = $\text{C}_6\text{H}_5\text{COCHCOCH}_3$, $n = 2$ (**9**); diket = $\text{C}_6\text{H}_5\text{COCHCOCH}_3$, $n = 1$ (**10**); diket = $\text{CF}_3\text{COCHCOOC}_6\text{H}_5$, $n = 2$ (**11**);
diket = $\text{CF}_3\text{COCHCOOC}_6\text{H}_5$, $n = 1$ (**12**); diket = $\text{CH}_3\text{COCHCOCH}_3$, $n = 0$ (**13**).

IR and MS analysis

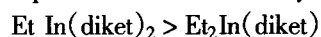
All compounds exhibit the characteristic $\text{C}=\text{O}$ and $\text{C}=\text{C}$ multiple absorption bands of O-chelate complexes at 1500—1600 cm^{-1} .⁸

Compounds **1**—**12** can be classified into two types: $\text{Et}_2\text{In}(\text{diket})$ and $\text{EtIn}(\text{diket})_2$. The mass spectra of

$\text{Et}_2\text{In}(\text{diket})$ showed signals of $\text{EtIn}(\text{diket})_2^+$ in addition to $\text{Et}_2\text{In}(\text{diket})^+$, Et_3In and $\text{In}(\text{diket})_3^+$. In contrast, the mass spectra of $\text{EtIn}(\text{diket})_2$ displayed signals of $\text{EtIn}(\text{diket})_2^+$, Et_3In^+ and $\text{In}(\text{diket})_3^+$. In view of the MS data of $\text{Et}_2\text{In}(\text{diket})$ and $\text{EtIn}(\text{diket})_2$, the disproportionation occurring at moderately high temperature presumably involved the following equilibria:



The sequence of thermal stability may be:



in the sequence of thermal stability:



Table 2 MS data for compounds (1–13) (EI, 150–250°C)

Compounds $\text{Et}_n\text{In}(\text{diket})_{3-n}$	Main peaks, m/z					
1	272(M)	243(M - Et)	214(M - 2Et)	173(M - diket)	202(Et_3In)	
	342[$\text{EtIn}(\text{diket})_2$]	144(M - Et - diket)	115(In)			
2	342(M)	313(M - Et)	214(M - Et - diket)	115(In)	202(Et_3In)	173(Et_2In)
	144(M - 2diket)	412[$\text{In}(\text{diket})_3$]				
3	332(M)	303(M - diket)	274(M - Et - diket)	202(Et_3In)	115(In)	433(M - Et)
	462[$\text{EtIn}(\text{diket})_2$]					
4	462(M)	274(M - 2Et)	303(M - Et)	202(Et_3In)	173(M - diket)	592[$\text{In}(\text{diket})_3$]
	433(M - Et)					
5	302(M)	273(M - Et)	244(M - Et - diket)	202(Et_3In)	115(In)	402[$\text{EtIn}(\text{diket})_2$]
6	402(M)	373(M - Et)	273(M - diket)	244(M - Et - diket)	202(Et_3In)	502[$\text{In}(\text{diket})_3$]
7	394(M)	365(M - Et)	336(M - 2Et)	173(M - diket)	586[$\text{EtIn}(\text{diket})_2$]	202(Et_3In)
	115(In)					
8	586(M)	557(M - Et)	365[M - diket]	336[M - Et - diket]	202(Et_3In)	778[$\text{In}(\text{diket})_3$]
	115(In)					
9	334(M)	305(M - Et)	173[M - diket]	115(In)	466[$\text{EtIn}(\text{diket})_2$]	202(Et_3In)
10	437(M - Et)	305(M - diket)	276(M - Et - diket)	202(Et_3In)	598[$\text{In}(\text{diket})_3$]	115(In)
11	388(M)	359(M - Et)	330(M - 2Et)	173(M - diket)	574[$\text{EtIn}(\text{diket})_2$]	202(Et_3In)
	115(In)					
12	574(M)	545(M - Et)	359(M - diket)	144(M - 2diket)	115(In)	760[$\text{In}(\text{diket})_3$]
13	412(M)	313(M - diket)	214(M - 2diket)	115(In)		

MS data are given for isotopes ^{115}In , ^{19}F , ^{12}C and ^{16}O . The peak patterns correspond to theoretical values based on the natural abundance of isotopes.

X-Ray crystallography

An ORTEP diagram of the molecular structure of **13** is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 3. The crystallographic data and structure refinement parameters are summarized in Table

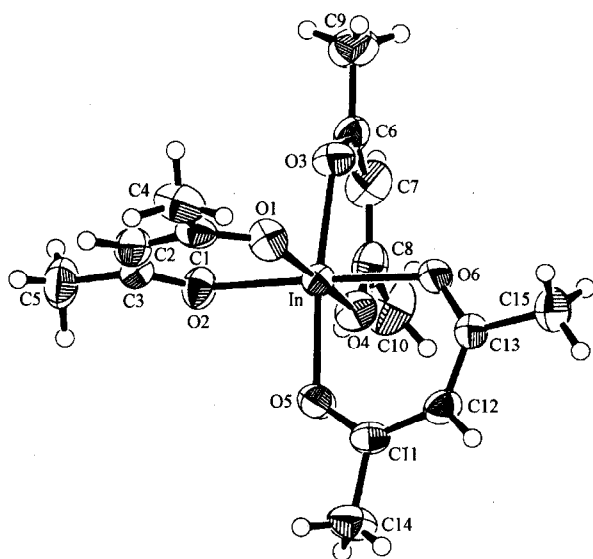
4. In the mononuclear indium complex, the central metal atom is coordinated by three acetylacetonato ligands in the bidentate fashion. The geometry around the indium atom of this structure can be described as distorted octahedral.

Table 3 Selected bond lengths (nm) and bond angle (deg)

Bond	Dist.	Angle	Deg	Angle	Deg
In—O1	0.2136(2)	O1-In-O2	85.48(9)	O2-In-O6	173.30(9)
In—O2	0.2128(2)	O1-In-O3	90.35(10)	O3-In-O4	85.61(10)
In—O3	0.2142(3)	O1-In-O4	172.30(10)	O3-In-O5	173.57(9)
In—O4	0.2127(2)	O1-In-O5	94.20(10)	O3-In-O6	88.93(9)
In—O5	0.2131(2)	O1-In-O6	91.07(10)	O4-In-O5	90.4(1)
In—O6	0.2120(2)	O2-In-O3	94.28(10)	O4-In-O6	95.40(10)
O1—C1	0.1261(4)	O2-In-O4	88.29(10)	O5-In-O6	86.46(9)
O2—C3	0.1265(4)	O2-In-O5	90.60(9)	In-O1-C1	127.6(2)

Table 4 Details of structure determination for **13**

Formula	C ₁₅ H ₂₁ O ₆ In
Formula weight	412.15
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (# 14)
Crystal colour, habit	colorless, prismatic
Unit cell dimensions(mm)	0.20 × 0.20 × 0.30
<i>a</i> , nm	0.8212(1)
<i>b</i> , nm	1.3277(1)
<i>c</i> , nm	1.6349(4)
β, deg	90.85(2)
<i>Z</i>	4
<i>V</i> , nm ³	1.7824(5)
<i>D</i> _{calc} (Mg/m ³)	1.536
μ (mm ⁻¹)	1.347
<i>F</i> (000)	832
Scan type	ω-2θ
<i>R</i> , <i>R</i> _w	0.026, 0.33

**Fig. 1** Molecular structure of $\text{In}(\text{CH}_3\text{COCHCOCH}_3)_3$ (**13**).

Experimental

All operations were performed under prepurified argon using Schlenk technique or in a glovebox. All solvents were refluxed and distilled over LiAlH_4 or sodium benzophenone under argon immediately before use. The liquid β -diketones were dried over anhydrous Na_2SO_4 and distilled under argon. The solid β -diketones were dried *in vacuo* for 4 h. Et_3In was prepared by a published procedure.⁹

General method of the synthesis of $\text{Et}_n\text{In}(\text{diket})_{3-n}$

To a suspension of Et_3In (1 equiv.) in benzene was added the β -diketone (1 or 2 or 3 equiv.) The reaction suspension gradually released a gas under stirring at room temperature. The solution was heated to 60°C and continuously stirred for 24 h, the benzene was removed *in vacuo*, and the resulting solid was recrystallized in petroleum ether/benzene (twice) to afford $\text{Et}_n\text{In}(\text{diket})_{3-n}$. Yields, analysis and physical properties of all **13** compounds are listed in Table 1.

Elemental analysis data were obtained with a Yanaco MT-2 analyzer. IR spectra were recorded on a Perkin-Elmer 983 (G) spectrometer. MS signals were recorded on an HP 5989A MS spectrometer. X-ray data were collected on a Rigaku AFC7R single crystal diffractometer.

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