

# The NaCl Adduct of the Iron-Indium Compound $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-InR})_2$ [ $\text{R} = \text{C}(\text{SiMe}_3)_3$ ] – a One-Dimensional Coordination Polymer with Sodium Oxygen Bridges

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The organoindium subhalide  $[\text{R}(\text{Cl})\text{In-In}(\text{Cl})\text{R}]_2$  [ $\text{R} = \text{C}(\text{SiMe}_3)_3$ ] **1** reacts with  $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$  to form an iron-indium coordination compound which was isolated as the sodium chloride adduct  $[\text{Na}(\text{THF})_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-InR})_2\text{Cl}]$  **2**. The iron atoms of **2** are bridged by a CO ligand and two InR groups, the indium atoms of which are further connected by the  $\mu_2$ -bridging chlorine atom. Four THF molecules and two oxygen atoms of terminal CO ligands of different anions span the coordination sphere of the sodium cations to give a one-dimensional coordination polymer in the solid state.

**Key words:** Indium, Iron, Coordination Compound

## Introduction

The tetrahedral tetraindium cluster  $\text{In}_4[\text{C}(\text{SiMe}_3)_3]_4$  is easily available by the reaction of indium(I) bromide with the corresponding alkylolithium compound [1]. It shows a remarkable chemical reactivity. For instance, subhalides such as  $\text{In}_2\text{Cl}_2\text{R}_2$  **1** and  $\text{In}_4\text{Br}_2\text{R}_4$  [2,3] were synthesized upon oxidation of the cluster with hexachloroethane, 1,2-dibromoethane or mixtures of bromine with aluminum tribromide, respectively. Furthermore, following the isolobal relationship between the monomeric cluster fragments InR and carbon monoxide, transition metal carbonyl analogous compounds were isolated in which bridging or terminal CO ligands are replaced by InR [4–8]. The most fascinating products of that type are the  $\text{Ni}(\text{CO})_4$  analogues  $\text{M}(\text{ER})_4$  ( $\text{M} = \text{Ni}, \text{Pt}$ ;  $\text{E} = \text{Ga}, \text{In}$ ), which possess exclusively terminally coordinated E-R groups. Their bonding situation is quite similar to that of the corresponding binary carbonyl complexes with a strong  $\pi$ -back bonding of electron density from the central nickel or platinum atoms into empty p-orbitals of the third main-group elements [5–7]. We hoped to isolate more of these carbonyl analogous compounds by the reaction of the subhalide **1** with carbonylate anions.

## Preparative Results

A solution of  $\text{R}(\text{Cl})\text{In-In}(\text{Cl})\text{R}$  **1** in *n*-pentane was treated with an excess of solid  $\text{Na}_2[\text{Fe}_2(\text{CO})_8] \cdot 4\text{THF}$ . The carbonylate is insoluble under these conditions, and the resulting suspension therefore was stirred for two weeks at room temperature. As was shown by NMR spectroscopy, mixtures of unstable and unknown intermediates were formed. However, we did not succeed in isolating any of these products by interrupting the reaction at an earlier stage. After filtration and concentration orange crystals of the product **2** (eq. (1)) were isolated in 55% yield. **2** decomposes above 127 °C with gas evolution. It was identified by a crystal structure determination as  $[\text{Na}(\text{THF})_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-InR})_2\text{Cl}]$  (see below). Owing to the lability of compound **2** the NMR spectra were recorded at low temperature in  $\text{D}_8\text{-THF}$ , but it was not possible to assign all resonances unambiguously. In the  $^{13}\text{C}$  NMR spectrum one resonance was observed at  $\delta = 221.2$  for carbonyl groups, and a poorly resolved further signal of low intensity was detected at  $\delta = 221.4$ , which, however, may be caused by decomposition products. Seven CO absorptions were found in the IR spec-

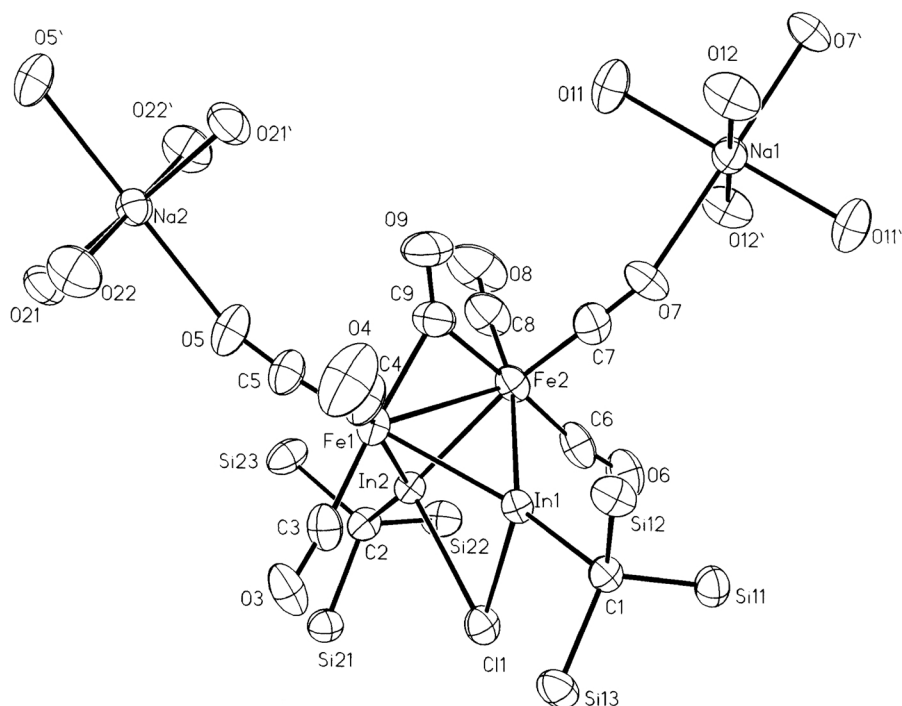
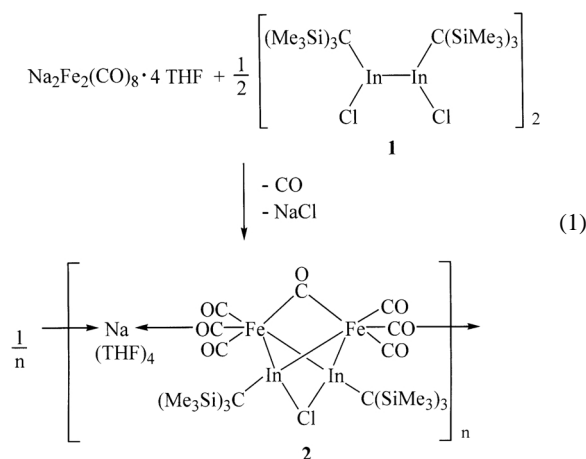


Fig. 1. Molecular structure of compound **2**. The ellipsoids are drawn at the 40% probability level; methyl groups are omitted; the sodium atoms reside on special positions, only the coordinating oxygen atoms of the THF molecules are shown. Selected bond lengths [pm] and angles [°]: Fe1–Fe2 274.8(2), Fe1–C3 180(1), Fe1–C4 176(1), Fe1–C5 176(1), Fe1–C9 195(1), Fe1–In1 263.6(2), Fe1–In2 263.9(2), Fe2–C6 176(1), Fe2–C7 177(1), Fe2–C8 177(1), Fe2–C9 202(1), Fe2–In1 263.1(2), Fe2–In2 264.3(2), In1–C1 221(1), In1–Cl1 272.2(3), In2–C2 226(1), In2–Cl1 272.0(3), Na1–O7 257.7(8), Na2–O5 255.3(9), Na–O(THF) 229.6(9)–235.9(9), In1–Cl1–In2 73.64(8), Fe1–In1–Fe2 62.90(5), Fe1–In2–Fe2 62.70(5), Fe1–C9–Fe2 87.7(5), C7–O7–Na1 144.7(9), C5–O5–Na2 151.0(9).



trum. One at  $1759 \text{ cm}^{-1}$  was assigned to the bridging carbonyl ligand. The other ones occur between  $1815$  and  $2001 \text{ cm}^{-1}$ . Their number verifies the particular molecular structure and symmetry of **2** in the solid state with the formation of one-dimensional co-

ordination polymers and sodium in bridging positions between oxygen atoms of terminal carbonyl groups. In particular the unusual absorption with the lowest wave number of that series ( $1815 \text{ cm}^{-1}$ ) may be taken as indicative of that bonding situation.

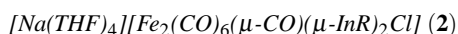
### Crystal Structure

The molecular structure and numbering scheme of compound **2** is depicted in Fig. 1. It contains a diiron moiety in its molecular center which is bridged by one carbonmonoxide and two InR ligands. Each iron atom is further attached to three terminal carbonyl groups. This part of the molecule is quite similar to that of the compound  $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-InR})_2]$  (**3**), which was obtained by the reaction of enneacarbonyldiiron with the tetraindium cluster [8] and which is isostructural with the starting carbonyl complex. The Fe–Fe separation in **2** [274.8(2) pm] is quite similar to that observed for **3**, but strongly elongated compared to the Fe–Fe distance in the isostructural pure carbonyl  $\text{Fe}_2(\text{CO})_9$

[252.2(1) pm] [9]. This difference may simply be caused by the different Fe-C and Fe-In bond lengths. The Fe-In distances of **2** [263.1(2) to 264.3(2) pm] are slightly lengthened by about 5 pm compared to those of **3**. They are in the range usually observed for Fe-In complexes [4, 8, 10]. The most interesting difference between **2** and **3** is the presence of one equivalent of sodium chloride in the structure of **2**. The chloride anion is in a bridging position between both indium atoms, which have distorted tetrahedral coordination spheres. The In-Cl distances are 272.1 pm on average, which correspond to weak bonding. In-Cl distances between 241 and 282 pm have been observed for dimeric or polymeric  $\text{R}_2\text{InCl}$  or  $\text{RInCl}_2$  compounds, the longer ones belonging to weak In-Cl interactions in polymeric dichlorides possessing pentacoordinated indium atoms with the corresponding chlorine atoms in axial positions [11, 12]. The angle In-Cl-In is rather acute with  $73.64(8)^\circ$ . By that bridging the indium atoms approach more closely to 326.2(1) pm compared to an In-In separation of 362 pm in **3** [8]. The smaller value is near the range of significant In-In interactions in cluster compounds of the monovalent element, in which distances of 300 to 315 pm have been detected [1]. Owing to the steric shielding by the bulky substituents the halide ion is not attached to sodium cations, which are located on inversion centers and possess a quite remarkable distorted octahedral coordination sphere consisting of six oxygen atoms. Four of these are in the equatorial plane and belong to THF molecules with normal Na-O distances in the range of 229.6(9) and 235.9(9) pm. Two longer distances to opposite oxygen atoms of 257.7(8) and 255.3(9) pm indicate an interaction between sodium and oxygen atoms of terminal CO ligands (O7 and O5). By these interactions one-dimensional coordination polymers are formed in the solid state. A similar coordination of terminal CO ligands by sodium has been observed for the starting dianion  $[\text{Na}(\text{THF})_2]_2[\text{Fe}_2(\text{CO})_8]$  [13], which forms a layer structure.

## Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane over  $\text{LiAlH}_4$ ). Dimeric dialkyldiindium dichloride **1** and  $[\text{Na}(\text{THF})_2]_2[\text{Fe}_2(\text{CO})_8]$  were synthesized according to literature procedures [3, 14].



A solution of the subhalide **1** (0.398 g, 0.522 mmol) in 30 ml of *n*-pentane was treated with an excess of

Table 1. Crystal data, data collection, and structure refinement for compound **2**.

Crystal data	
Empirical formula	$\text{C}_{43}\text{H}_{86}\text{ClFe}_2\text{In}_2\text{NaO}_{11}\text{Si}_6$
$M_r$	1347.44
Crystal system	triclinic
Space group	$P\bar{1}$ ; no. 2 [16]
$a$ (pm)	1347.9(1)
$b$ (pm)	1354.5(1)
$c$ (pm)	1952.8(2)
$\alpha$ ( $^\circ$ )	90.139(7)
$\beta$ ( $^\circ$ )	90.752(7)
$\gamma$ ( $^\circ$ )	118.551(6)
$V(\text{\AA}^3)$	3131.3(5)
$\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.429
$Z$	2
$F(000)$	1388
$\mu(\text{Mo-K}\alpha)$ ( $\text{cm}^{-1}$ )	13.92; numerical absorption correction
Data collection	
$T$ (K)	193(2)
Measured reflections	42116
Unique reflections	12485 [ $R_{\text{int}} = 0.0643$ ]
Reflections $I > 2\sigma(I)$	9128
Refinement	
Refined parameters	611
Final $R$ values [ $I > 2\sigma(I)$ ]	
$R1^{[a]}$	0.0783
$wR2^{[b]}$ (all data)	0.2382
$\rho_{\text{fin}}(\text{max/min}) (\text{e}\text{\AA}^{-3})$	1.487/−1.372
[a] $R = \Sigma  F_o  -  F_c   / \Sigma F_o $ ; [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ .	

$[\text{Na}(\text{THF})_2]_2[\text{Fe}_2(\text{CO})_8]$  (0.797 g, 1.19 mmol). The suspension was stirred at room temperature for two weeks. After filtration the solution was concentrated in vacuum to 8 ml and cooled to  $5^\circ\text{C}$ . Orange crystals of **2** precipitated within two days (0.385 g, 55%). Dec. p. (under argon, sealed capillary):  $127^\circ\text{C}$ . – IR ( $\text{cm}^{-1}$ ; paraffin; CsBr plates): 2001 s, 1966 m, 1932 s, 1900 sh, 1876 m, 1815 m  $\nu\text{CO}$  (terminal); 1759 m  $\nu\text{CO}$  ( $\text{Fe}_2\text{CO}$  bridge); 1461 vs, 1377 vs paraffin; 1293 w, 1259 s, 1251 s  $\delta_s\text{CH}_3$ ; 1170 w, 1051 m THF; 857 vs, 840 vs, 776 w  $\rho\text{CH}_3$ ; 723 w paraffin; 677 w  $\nu_{\text{as}}\text{SiC}_3$ ; 633 s, 608 m, 592 m  $\nu_s\text{SiC}_3$ ,  $\nu\text{FeC}$ . –  $^1\text{H}$  NMR (400 MHz,  $\text{D}_8\text{-THF}$ , 253 K):  $\delta = 0.30$  (54 H, s,  $\text{SiMe}_3$ ), 1.82 (16 H, m,  $\text{CH}_2$  of THF), 3.66 (16 H, m,  $\text{OCH}_2$  of THF). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{D}_8\text{-THF}$ , 253 K):  $\delta = 6.5$  ( $\text{SiMe}_3$ ), 26.3 (THF), 68.1 (THF), 221.2 (Fe-CO); InC not detected.

## Crystal structure determination

Single crystals of compound **2** were obtained by cooling of a saturated solution in *n*-pentane to  $5^\circ\text{C}$ . Data collection was performed on a STOE IPDS diffractometer employing graphite-monochromated Mo- $\text{K}\alpha$  radiation. The structure

was solved by direct methods and refined by a full matrix least-squares calculation based on  $F^2$  [15]. The hydrogen atoms were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. Crystallographic data for the structure **2** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC-199450. Copies of the data can be obtained free of charge on application to

The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk)

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