The Anion $[Co(C_8H_{12})_2]^-$. A Comparative Study of the Crystal Structures of $[\{K(18\text{-crown-6})\}_2(C_5H_5)][Co(C_8H_{12})_2]$ and $Co(C_8H_{12})(C_8H_{13})$

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The cobalt complex $[\{K(18\text{-crown-6})\}_2(C_5H_5)]$-$[Co(C_8H_{12})_2]\cdot(THF)_2$ (**3**) has been synthesized and characterized by X-ray single-crystal structure determination. The crystal structure of $Co(C_8H_{12})(C_8H_{13})$ (**2**) has been reinvestigated and compared with the structure of **3**. The 1,5-cyclooctadiene (C_8H_{12}) and C_8H_{13} ligands are coordinated in an η^4 and η^3 fashion, respectively. The cyclopentadienyl anion in $[\{K(18\text{-crown-6})\}_2(C_5H_5)]^+$ in **3** is η^5-coordinated to the two crown ether-encapsulated potassium cations.

Key words: Synthesis, Crystal Structure, Cobalt Complex

Introduction

Many low-valent transition metal complexes containing 1,5-cyclooctadiene (C_8H_{12}, 1,5-cod) as π-coordinated ligand have been prepared during the last 40 years [1]. Some of them, *e. g.* $[Rh_2Cl_2(C_8H_{12})_2]$[2a], $[Ir_2Cl_2(C_8H_{12})_2]$ [2b, 2c], $[Pt(C_8H_{12})_2]$ [2d], and $[Ni(C_8H_{12})_2]$ (**1**) [2e, 2f], are widely used as starting materials in organometallic chemistry. The cod ligands are good leaving groups and can easily be replaced by other donors, such as phosphines, phoshites and many others. This property is helpful in materials chemistry for producing "naked" metal atoms [3]. Recently, some "ligand-free" endohedral Zintl clusters were obtained through the reactions of $[Ni(C_8H_{12})_2]$ (**1**) with K_4Ge_9, K_4Sn_9, or K_4Pb_9, such as $[Ni@Ge_9]^{3-}$ [4], $[(Ni@Ge_9)Ni(Ni@Ge_9)]^{4-}$ [4], $[(Ni@Sn_8)Sn(Ni@Sn_8)]^{4-}$ [5], $[Ni@Pb_{10}]^{2-}$ [6], $[Ni@Pb_{12}]^{2-}$ [7], and even larger clusters such as $[As@Ni_{12}@As_{20}]^{3-}$ can be prepared by the reaction of $[Ni(C_8H_{12})_2]$ (**1**) with As_7^{3-} [8]. In contrast to **1**, the 1,5-cod-coordinated complex $Co(C_8H_{12})(C_8H_{13})$ (**2**) is still not widely used for cluster formation, even though the synthesis of **2** was reported already in 1968 and was achieved by reaction of anhydrous cobalt dichloride with sodium [9] or tris(acetylacetonato)cobalt(III) with dialkylaluminum hydrides [10]. Up to now, there is no crystallographic proof of the existence of the analogous neutral $[Co(C_8H_{12})_2]$ molecule, but the structure of the $[Co(C_8H_{12})_2]^-$ (**3a**) anion in $Li(THF)_2[Co(C_8H_{12})_2]$, which is similar to that of **1**, was reported in 1976 by Jonas *et al.* [11]. Thirty years later, another synthesis of **3a** was reported by J. E. Ellis *et al.*, but no crystal structure was described in this work [12].

We found that $Co(C_8H_{12})(C_8H_{13})$ (**2**) can be used as a storable source of a cobalt atom in the synthesis of the endohedral Zintl cluster $[Co@Ge_{10}]^{3-}$ [13]. More important, we also found that the anion $[Co(C_8H_{12})_2]^-$ (**3a**) was formed during the reactions, which co-crystallized together with $[Co@Ge_{10}]^{3-}$ in the form of $[K(2,2,2\text{-crypt})]_4[Co@Ge_{10}][Co(C_8H_{12})_2]$ (**4**) [13]. In order to elucidate the source and the structure of 1,5-cod-coordinated cobalt complexes and to assign the ^{59}Co NMR signals to the units in **4**, we synthesized the neutral compound $Co(C_8H_{12})(C_8H_{13})$ (**2**) and the anionic species $[Co(C_8H_{12})_2]^-$ (**3a**). The latter was isolated as $[\{K(18\text{-crown-6})\}_2(C_5H_5)]$-$[Co(C_8H_{12})_2]\cdot(THF)_2$ (**3**) and structurally characterized. Since for **2** no satisfactory structural refinement was available so far ($R1$ = 12.5 %) [9], we reinvestigated the molecular structure of **2** by means of single crystal X-ray diffraction and report on the ^{59}Co NMR spectra of **2** and **3**.

Results and Discussion

A solution of Cp_2Co and 1,5-cod in THF reacts with potassium naphthalide in THF in the presence of 18-crown-6 to give an air-sensitive orange solid. After recrystallization from THF / hexane, orange crystals of $[\{K(18\text{-crown-6})\}_2(C_5H_5)][Co(C_8H_{12})_2]\cdot(THF)_2$ (**3**) could be isolated. The ^{1}H NMR spectrum of **3** in solution is entirely consistent with the formula, and shows resonances characteristic of η^4-1,5-cod, Cp, and 18-crown-6 entities. A single-crystal X-ray study on **3** revealed the presence of the anion **3a** which crystallizes with two $[K(18\text{-crown-6})]^+$ cations and one $C_5H_5^-$ anion in the monoclinic space group $P2_1/c$.

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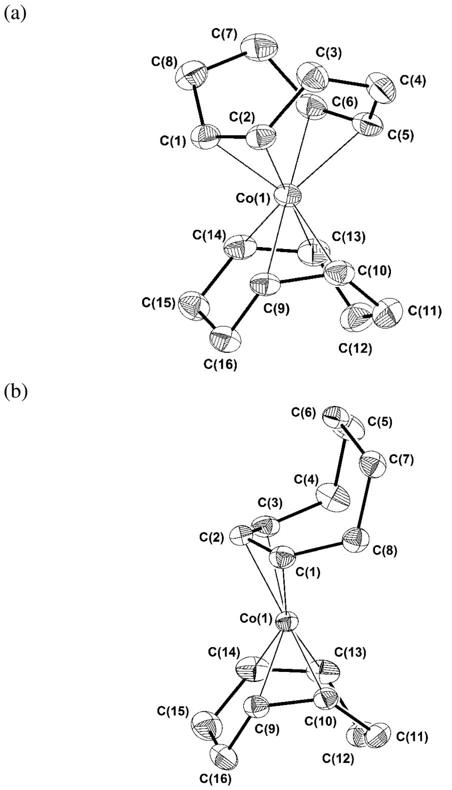

Fig. 1. Structures of the $[Co(C_8H_{12})_2]^-$ anion (**3a**) (a) and of $Co(C_8H_{12})(C_8H_{13})$ (**2**) (b), Displacement ellipsoids are set at the 50 % probability level, with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): **3a** Co(1)–C(1) 2.045(4), Co(1)–C(5) 2.047(4), Co(1)–C(9) 2.029(4), Co(1)–C(13) 2.031(4), C(1)–C(2) 1.408(6), C(5)–C(6) 1.409(6), C(9)–C(10) 1.409(6), C(13)–C(14) 1.411(6); C(1)–Co(1)–C(2) 40.4(2), C(9)–Co(1)–C(10) 40.6(2); **2** Co(1)–C(1) 2.063(2), Co(1)–C(2) 2.016(2), Co(1)–C(3) 2.075(2), C(1)–C(2) 1.403(2), C(2)–C(3) 1.401(3), C(3)–C(4) 1.516(3), C(4)–C(5) 1.538(3), Co(1)–C(9) 2.0372(18), Co(1)–C(13) 2.0437(18), C(9)–C(10) 1.397(2), C(13)–C(14) 1.396(3); C(1)–Co(1)–C(2) 40.21(7), C(2)–Co(1)–C(3) 40.02(7), C(9)–Co(1)–C(10) 40.20(7).

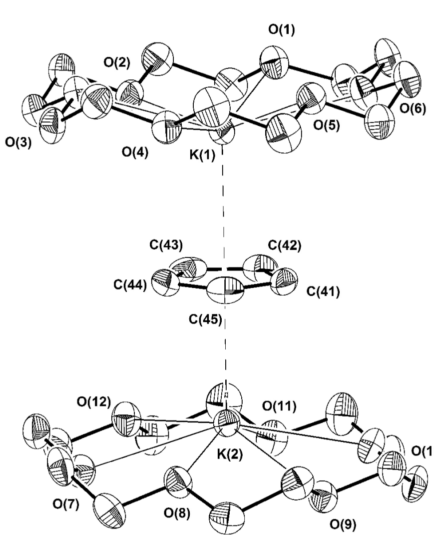

Fig. 2. Structure of $[\{K(18\text{-crown-}6)\}_2(C_5H_5)]^+$ (**3b**). Displacement ellipsoids are set at the 50 % probability level, with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): K(1)–O(18-crown-6) 2.797(3)–2.950(3), K(1)–C(Cp) 3.026(4)–3.107(5), K(2)–O(18-crown-6) 2.822(3)–2.934(3), K(2)–C(Cp) 3.016(5)–3.111(4), C(Cp)–C(Cp) 1.373(7)–1.400(6), K(1)–$Cp_{centroid}$ 2.821, K(2)–$Cp_{centroid}$ 2.829; K(1)–C(Cp)–K(2) 130.4(2)–138.1(2), C(45)–C(41)–C(42) 108.0(4), C(41)–C(42)–C(43) 107.9(4), C(42)–C(43)–C(44) 108.3(4), C(43)–C(44)–C(45) 107.7(4), C(44)–C(45)–C(41) 108.1(4).

The cobalt atom of **3a** is sandwiched by two 1,5-cod rings (C_8H_{12}) (see Fig. 1a). These two rings adopt a boat conformation, in which the C=C double bonds are coordinated to the cobalt atom in a similar way as observed in the structure of **1**. The twist angle of 53° between the two 1,5-cod rings in **3a** is smaller than the one observed in **1** (the corresponding angle is 73°) [2f], but much closer to the one in the anion **4** with a twist angle of 55° [13]. The cod ligand in **2** is coordinated with a similar boat conformation as the one in **3a**, whereas the C_8H_{13} ligand adopts a tub-like form with η^3-cyclooctenyl coordination (see Fig. 1b). Interatomic distances between the metal atom Co(1) and the eight coordinated carbon atoms in **3a** are in the same range from 2.029(4) to 2.047(4) Å as those in **2** (2.016(2) to 2.075(2) Å). The average bond length of the four double bonds in **3a** is 1.41 Å, and the corresponding bond lengths in **2** are only marginally shorter than those in **3a**.

The fragment $[\{K(18\text{-crown-}6)\}_2(C_5H_5)]^+$ (**3b**) in the crystal of compound **3** consists of two $[K(18\text{-crown-}6)]^+$ cations and one $C_5H_5^-$ anion. The central cyclopentadienyl anion is η^5-coordinated to the two crown ether-encapsulated potassium cations (Fig. 2). Each K^+ cation is connected to the six O atoms of the 18-crown-6 ligands and to five C atoms of the $C_5H_5^-$ anion. The K–C distances range from 3.016(5) to 3.111(4) Å, and the distances between the center of the Cp ring and the two K atoms are 2.821 and 2.829 Å, respectively, similar to the distances reported for other compounds containing the CpK fragement, such as polymeric KCp (K–$Cp_{centroid}$ 2.816 Å) [14], and $[K(18\text{-crown-}6)](C_5H_5)$ (K–$Cp_{centroid}$ 2.819 Å) [15]. The C–C bond lengths in the Cp ligand range from 1.373(7) to 1.400(6) Å. 18-Crown-6 is well known as an effective sequestering agent for cations thereby stabilizing organic anions as *e. g.* in [K(18-crown-6)]($C_{10}H_{15}$) [15], [K(18-crown-6)](C_7H_8) [16], or [K(18-crown-6)]$_2$($C_{28}H_{40}$) [17].

Due to the relatively high magnetic moment and a natural abundance of 100 % of the quadrupolar nucleus, a large number of ^{59}Co NMR data are available [18]. The ^{59}Co NMR resonance of anion **3a** appears as a single, broad signal at -1737 ppm ($\Delta_{V1/2}$ = 1376 Hz, at 25 °C), while the signal of compound **2** is observed at -280 ppm, in accordance with reported data [18].

In order to investigate the relationship between $[Co(C_8H_{12})_2]^-$ and $Co(C_8H_{12})(C_8H_{13})$, several experiments were performed. $Co(C_8H_{12})(C_8H_{13})$ was reacted with different agents, such as Na, Mg, Zn, and $KC_{10}H_8$ under different conditions. It was found that, in the presence of 1,5-cod, $Co(C_8H_{12})(C_8H_{13})$ can be deprotonated by $KC_{10}H_8$. The resulting mixture was characterized by ^{59}Co NMR spectroscopy, and one new signal appeared at *ca.* -1730 ppm, which resembles that observed for $[Co(C_8H_{12})_2]^-$ (**3a**). Due to a low conversion, it was difficult to obtain larger amounts of pure samples containing the $[Co(C_8H_{12})_2]^-$ anion from the mixture with the starting material $Co(C_8H_{12})(C_8H_{13})$. This may also explain the appearance of the $[Co(C_8H_{12})_2]^-$ (**3a**) anion in the reaction of $Co(C_8H_{12})(C_8H_{13})$ with the highly reducing compound K_4Ge_9 [13].

Experimental Section

All manipulations and reactions were performed in an Ar atmosphere, using standard Schlenk line or glove box techniques. THF, hexane, toluene, and diethyl ether (Merck, 99 %) were used after purification. 18-Crown-6 (Merck) was recrystallized under vacuum. Cp_2Co [19], $KC_{10}H_8$ (prepared from K and $C_{10}H_8$ in THF at ratio 1 : 1), and $Co(C_8H_{12})(C_8H_{13})$ (**2**) [9] were prepared according to reported methods. Suitable single crystals were obtained from hexane at −28°C. The ^{59}Co NMR spectra of compounds **2** and **3** were recorded on a Bruker AMX400 instrument with a 10 mmol L^{-1} solution of single crystals in THF at 94.9 MHz and referenced to $K_3[Co(CN)_3]$ in D_2O as external standard at T = 298 K. A total of 2000 scans were accumulated.

Preparation of $[\{K(18\text{-crown-6})\}_2(C_5H_5)][Co(C_8H_{12})_2] \cdot (THF)_2$ *(3)*

Cp_2Co (10 mmol, 1.89 g) and 1,5-cod (30 mmol, 3.7 mL) were dissolved in THF (50 mL). The red solution was cooled below 0 °C and slowly transferred to a dark-blue solution of $KC_{10}H_8$ (25 mmol) in THF (20 mL, −78 °C). The resulting red-brown solution was stirred for 10 h below 0 °C. After the solvent was removed under vacuum, the residue was washed with diethyl ether (10 mL). The brown solid was dissolved in THF (20 mL) and then transferred to a flask with asolution of 18-crown-6 (2.64 g, 10 mmol) in THF (5 mL). The mixture was stirred for 2 h and then concentrated to 5 mL. After layering with hexane (5 mL), yellow crystals of **3** (3.93 g, 36 %) formed at −70 °C. – ^{1}H NMR (400 MHz, TMS, [D$_8$]THF): δ = 2.14, 2.34 (br, 16H, CH_2CH_2), 4.33, 4.60 (br, 8H, $CHCH$), 3.54 (s, 48H, OCH_2), 5.63 (s, 5H, C_5H_5). – Elemental analysis for $C_{45}H_{77}O_{12}CoK$: calcd. C 59.52, H 8.55; found C 59.18, H 8.58.

X-Ray diffraction

Single-crystal X-ray diffraction data for $Co(C_8H_{12})(C_8H_{13})$ (**2**) and $[\{K(18\text{-crown-6})\}_2(C_5H_5)][Co(C_8H_{12})_2] \cdot (THF)_2$ (**3**) were collected on an Oxford Diffraction Xalibur3 diffractometer at T = 150 K with MoK_α radiation. The crystals were selected under Paratone-N oil and mounted on a glass fiber. The structures were solved by Direct Methods and refined on F^2 using the SHELXTL (version 6.1) package [20]. Crystal data for **2**: M_r = 276.29, space group $P2_1/c$, a = 10.5889(3), b = 7.3371(2), c = 17.6592(4) Å, β = 104.220(2)°, V = 1329.94(6) Å^3; Z = 4, ρ_{calcd} = 1.38 g cm^{-3}, μ = 1.3 mm^{-1}. 5231 measured reflections, 2361 independent reflections, R_{int} = 0.0147; $R1$ = 0.0276 and $wR2$ = 0.0701 for $I \geq 2\sigma(I)$, $R1$ = 0.0362 and $wR2$ = 0.0739 for all data. Crystal data for **3**: M_r = 1091.40, space group $P2_1/c$, a = 9.340(1), b = 25.6079(3), c = 25.8367(3) Å, β = 90.992(1)°, V = 6178.51(1) Å^3; Z = 4, ρ_{calcd} = 1.17 g cm^{-3}, μ = 0.5 mm^{-1}. 10845 measured reflections, 7842 independent reflections, R_{int} = 0.0386; $R1$ = 0.0643 and $wR2$ = 0.2186 for $I \geq 2\sigma(I)$, $R1$ = 0.0841 and $wR2$ = 0.2319 for all data.

CCDC 702925 and 702926 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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