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Preliminary communication

Reductive elimination of dimethylcarbonate from (dimethoxycarbonyl)tricarbonyl cobaltates. Isolation and crystal structures of $\text{Cs}[\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]$ and $\text{K}[(\text{dibenzo-18-crown-6})][\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]$ *

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Abstract

Salts of the anion $[\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]^-$ with Cs^+ and K^+ (with the latter cation complexed by dibenzo-18-crown-6 ether) have been isolated and structurally characterized. In the trigonal bipyramidal cobaltate two C-coordinated COOCH_3 groups occupy *trans*-axial positions. There are ionic interactions between the cation and the terminal oxygen atoms of methoxycarbonyl involving both of the coordinated COOCH_3 groups in the case of the Cs salt but only one of them in the case of the K salt. One methoxy group of the anion $[\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]^-$ is strongly nucleophilic, as shown by the reactions with $\text{Co}_2(\text{CO})_8$ or CO_2 . Under an inert atmosphere $[\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]^-$ undergoes elimination of dimethylcarbonate.

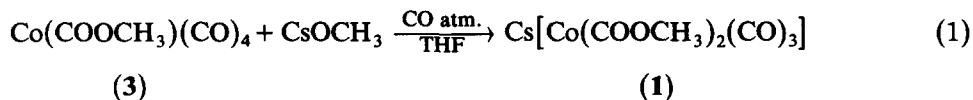
The oxidative carbonylation of alcohols to give dialkyloxalates represents a step in a syngas-based route to ethylene glycol. The alcohol/CO coupling has been accomplished only with palladium-based catalysts and the intermediates appear to be (dialkoxycarbonyl)-complexes that can undergo reductive elimination of dialkyl oxalates [1]. Most often, however, the elimination of dialkyloxalates requires the action of oxidizing agents, which also give some organic side products [2,3].

We now report the isolation and the characterization of the anionic (dialkoxycarbonyl)-complex $[\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]^-$ as its cesium (1) and potassium [dibenzo-18-crown-6] (2) salt, and on the selective elimination of dimethylcarbonate from it.

Compound 1 is formed in quantitative yield by adding CsOCH_3 to a THF solution of $\text{Co}(\text{COOCH}_3)(\text{CO})_4$ (3) [4] at room temperature under a CO atmosphere

* Dedicated to the memory of Piero Pino.

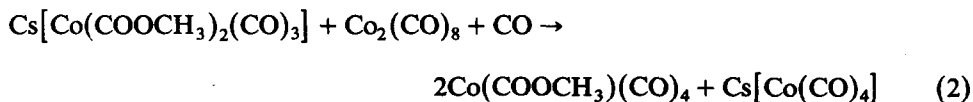
(eq. 1). Colorless crystals are obtained by adding $(C_2H_5)_2O$ to the solution. Pályi et al. [5] previously suggested the existence of the anion **1** on the basis of IR spectroscopy after they carried out a reaction similar to eq. 1 but with $NaOCH_3$ in the presence of 15-crown-5. However, further characterization was prevented by the fast thermal decomposition of the product. It is now evident that the stability of **1** is strongly dependent upon the CO pressure and on the nature of the cation.



The structure of $Cs[Co(COOCH_3)_2(CO)_3]$ was determined by X-ray diffraction [6*]. Each anion (Fig. 1) is almost trigonal bipyramidal, with two η^1 -coordinated alkoxycarbonyl groups in axial positions. The average $Co-COOCH_3$ bond, 1.96(2) Å, is ca. 0.2 Å longer than the average $Co-CO$ bond, suggesting that there is very little $Co(d_\pi)-C(p_\pi)$ interaction with the alkoxycarbonyl groups. Although the two CO_2 planes are skew by ca. 30° , the two methoxy groups are closer to an eclipsed than to a staggered disposition. This is probably a consequence of the stabilizing ionic interactions that each Cs^+ cation forms with the terminal oxygen atoms of $COOCH_3$ from four different complex anions. The contacts are short [in the range 3.00(1) and 3.07(1) Å] and involve equally the *trans*-methoxycarbonyl groups of any anion. The latter feature is fully consistent with the unique broad band at ca. $1610\ cm^{-1}$ observed in the IR spectrum of the solid.

By contrast this band is split into two bands (at 1600 and $1635\ cm^{-1}$) in the spectrum recorded for a THF solution of **1**, suggesting that only one methoxycarbonyl group is preferentially involved in ion pairing. To confirm this we also studied the structure [8*] of $[K(dibenzo-18-crown-6)][Co(COOCH_3)_2(CO)_3]$ (**2**), which in the solid state shows IR bands at 1600 and $1625\ cm^{-1}$. The gross structural features of cobaltate in **2** are not very different from those in **1** (Fig. 2), but it is evident that a terminal oxygen atom of a $COOCH_3$ group forms a bond with the K^+ ion surrounded by the crown ether [$K-O(5) = 2.77(1)\ \text{\AA}$]. The $Co-C-O-K$ bonding network compares well with that present in the compound $[Co(^nPr-salen)K(CO_2)(THF)_n]$, a rare $M-\eta^1-CO_2$ adduct [9]. In **2** the *trans*-axial $COOCH_3$ groups are almost staggered, and the group free from ion pairing with K^+ can strongly vibrate, as shown by the appearance of two peaks for the terminal oxygen atom in the ΔF maps.

Neutral (dialkoxycarbonyl)-complexes lose one methoxy group when reacted with strong electrophiles such as $CF_3SO_3CH_3$ and C_3SO_3H [10]. In the case of **1** one methoxy group leaves readily, and is strongly nucleophilic; e.g., **1** reacts with equimolar amounts of $Co_2(CO)_8$ in THF solution under a CO atmosphere to give $[Co(CO)_4]^-$ and **3** (see eq. 2).



* Reference number with asterisk indicates a note in the list of references.

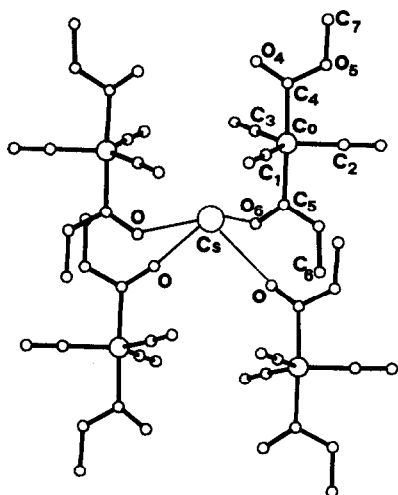


Fig. 1. A cesium cation forms short contacts [in the range 3.00–3.07(9) Å] with terminal oxygen atoms of methoxycarbonyl groups from four different $[\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]^-$ anions. Selected bond distances (Å): Co–C(1) 1.76(2), Co–C(2) 1.80(2), Co–C(3) 1.75(2), Co–C(4) 1.96(1), Co–C(5) 1.96(1), C–O (carbonyl) 1.15(3) ave., C(4)–O(4) 1.21(2), C(4)–O(5) 1.37(2), C(5)–O(6) 1.24(1), C(5)–O(7) 1.33(1), C(6)–O(7) 1.46(1). Angles ($^\circ$): C(4)–Co–C(5) 177.7(5), O(4)–C(4)–O(5) 118.6(1.1), O(6)–C(5)–O(7) 119.0(1.1), C(4)–O(5)–C(7) 118.4(1.0), C(5)–O(7)–C(6) 117.4(1.1).

Furthermore, a THF solution of **1** reacts instantaneously with carbon dioxide to give **3**, along with a precipitate of CsOCOOCH_3 .

Finally, **1** undergoes selective elimination of dimethylcarbonate (eq. 3). The reaction is complete in 3 hours at room temperature under an inert atmosphere; it is

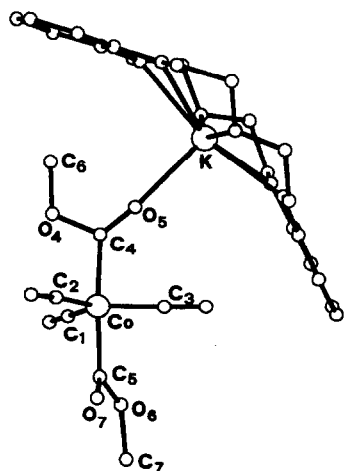


Fig. 2. Drawing of the adduct $[\text{K}(\text{dibenzo-18-crown-6})][\text{Co}(\text{COOCH}_3)_2(\text{CO})_3]$ (**2**). Selected bond distances (Å): Co–C(1) 1.83(2), Co–C(2) 1.80(2), Co–C(3) 1.78(2), Co–C(4) 1.97(1), Co–C(5) 1.93(3), C–O (carbonyl) 1.10(3) ave., C(4)–O(4) 1.37(2), C(4)–O(5) 1.19(2), C(5)–O(6) 1.29(1), C(5)–O(7) 1.43(4), C(7)–O(6) 1.44(2). Angles ($^\circ$): C(4)–Co–C(5) 175.2(8), O(4)–C(4)–O(5) 117(2), O(6)–C(5)–O(7) 116(2), C(4)–O(4)–C(6) 116(2), C(5)–O(6)–C(7) 122(2).

first order with respect to **1** and is inhibited by CO. These features favour the intermediacy of a methoxy(methoxycarbonyl)cobalt tricarbonyl complex formed by loss ("deinsertion") of CO from the CH₃OOC ligand in **1**.



Supplementary material. Lists of atomic coordinates, and bond distances and angles will be deposited with Cambridge Crystallographic Data Center.

References and notes

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- 6 *Crystal data* C₇H₆O₇Co₁CS₁: *M* = 393.96, monoclinic, *P*2₁/*c*, *a* = 11.868(4), *b* = 13.611(5), *c* = 7.634(3) Å, β = 104.07(2)°, *V* = 1196.27 Å³, *Z* = 4, *d*_{calc} = 2.187 g cm⁻³, *F*(000) = 744, λ(Mo-K_α) = 0.7107, μ(Mo-K_α) = 44.2. A crystal, sealed in a capillary with dimensions 0.1 × 0.2 × 0.3 mm³ was mounted on a CAD4 diffractometer. Intensities were collected up to 2θ = 60° [3803 measured reflections of which 1251 had intensities *I* > 3σ(*I*)]. The structure was solved by Patterson and Fourier methods. Empirical absorption corrections were made [7] with min.–max. absorption of 0.69–0.89. All of the non-hydrogen atoms were refined anisotropically. Final *R* and *R*_w values were 0.049 and 0.051, respectively.
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- 8 *Crystal data* C₂₇H₃₀O₁₃Co₁K₁: *M* = 660.56, triclinic *P*1̄, *a* = 15.955(4), *b* = 11.208(5), *c* = 9.435(3) Å, α = 66.53(2), β = 77.97(2), γ = 80.64(2)°, *V* = 1507.6 Å³, *Z* = 2, *d*_{calc} = 2.910 g cm⁻³, *F*(000) = 1368, λ(Cu-K_α) = 1.5418, μ(Cu-K_α) = 129.2. A crystal, sealed in a capillary with dimensions 0.1 × 0.1 × 0.2 mm³ was mounted on a PW 1100 diffractometer. Intensities were collected up to 2θ = 110° [3600 measured reflections, of which 1881 had intensities *I* > 3σ(*I*)]. The structure was solved by Patterson and Fourier methods. The empirical absorption coefficients, [7] are in the range 0.49–0.89. Co, K, O atoms were refined anisotropically. The present *R* and *R*_w values are 0.098 and 0.090, respectively. Attempts are still being made to solve the disorder associated with O7 (O8) atom.
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