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ARTICLE TYPE

Facile Insertion of CO₂ into Metal-Phenoxide Bonds

Sait Elmas, Muhammad Afzal Subhani, Henning Vogt, Walter Leitner and Thomas E. Müller*^a

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Supplementary data

Experimental

Methods

IR spectra were recorded *in-situ* with a Bruker MATRIX-MF spectrometer equipped with a high-pressure 3.17 mm ATR-IR fibre optical probe. The ATR-IR fibre optical probe (90° diamond prism with 1 × 2 mm basal area and 1 mm height as ATR element, 2 × 45° reflection of the IR beam, IR beam coupled *via* fibre optics) was fitted into the reactor in such a way that the diamond at the end of the optical probe was immersed entirely into the reaction mixture. IR spectra (average of 100 scans) were recorded time-resolved in the region 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹ against a solution of complex **1** or **2** in the respective solvent (difference spectra). The spectra were analysed with the software PEAXACT. The ¹H-NMR spectra were measured at 400 MHz using a Bruker AV400 spectrometer. Chemical shifts are reported relative to tetramethylsilane (TMS). Deuterated solvents were used as obtained.

Materials

All chemicals were obtained from commercial suppliers and used as received, if not stated otherwise. Complexes **1** and **2** as well as the chloro-complex corresponding to **1** were synthesised and characterised according to the procedures reported in the literature.^[1,2]

Activation of CO₂ by complex **1**.

A 160 ml stainless steel autoclave was charged with a solution of Co(III)-Salen complex **1** (15 mg, 0.02 mmol) in dichloromethane (20 ml). The reactor was pressurized with argon (3 bar) at room temperature and a background spectrum was recorded with *in-situ* ATR-IR spectroscopy. The pressure was released and the autoclave re-pressurized stepwise with respectively 4, 10, 20 and 30 bar CO₂ at room temperature. After each step, IR spectra were recorded until no further change was observed.

Activation of CO₂ by complex **2**.

A 160 ml stainless steel autoclave was charged with a solution of binuclear zinc complex **2** (15 mg, 0.02 mmol) in toluene (12 ml). After purging with argon, the reactor was heated to 90 °C, pressurized with argon (3 bar), and a background spectrum was recorded with *in-situ* ATR-IR spectroscopy. The pressure was released, and the autoclave was re-pressurized stepwise with 5,

13, 20 and 30 bar CO₂ at room temperature. Subsequently, the autoclave was cooled to ambient temperature, and the pressure was decreased stepwise from 30 bar to 21, 15, 10, 5 and 1 bar. Finally, the partial pressure of CO₂ was decreased to zero. After each step, IR spectra were recorded. The scan rates and the number of scans after each pressure increment are given in Table S1.

Table S1: Parameters and settings for recording the IR spectra during the reaction of **2** with CO₂.

Temperature [°C]	Partial pressure of CO ₂ [bar]	Number of scans	Scan rate [1/min]
90	5	15	1
90	13	15	1
90	21	15	1
90	30	45	1
20	21	15	2
20	15	10	2
20	10	10	2
20	5	10	2
20	1	10	2
20	0	15	2

Additional data

The ¹H-NMR spectrum of complex **1** in dimethylsulfoxide-d₆ is shown in Fig. S1.

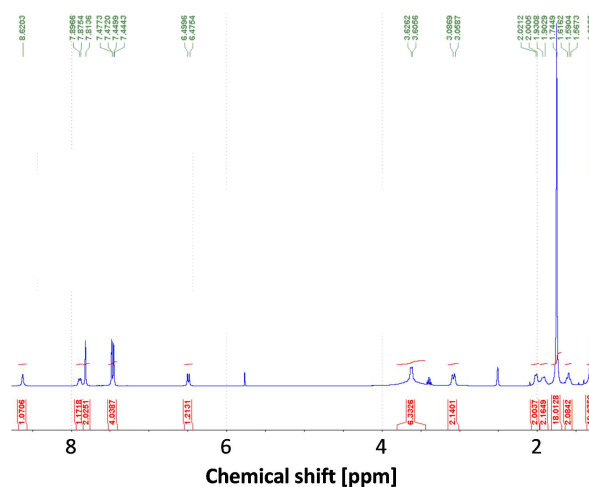
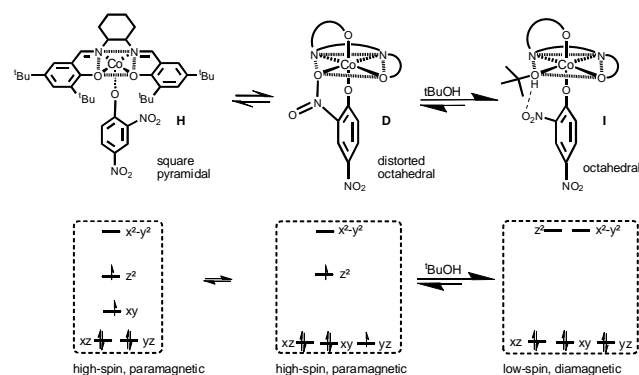


Fig. S1 ¹H-NMR spectrum of diamagnetic complex **1** in dimethylsulfoxide-d₆.

An analysis of the electron configuration of Co(III)-Salen complex **1** in dependence of the coordination geometry of the cobalt-centre is shown in Scheme S1.



Scheme S1 Possible coordination geometries of the d^6 Co(III) complex **1** leading to para- and diamagnetic states.

The structures **J**, **K**, **L** and **M** (Table S2) are selected examples found during a search of the Cambridge Crystallographic Database (CSD)³ for Co(III)-Salen complexes, whereby ConQuest was used as search tool.⁴

Table S2: Coordination geometries of selected Salen complexes.

No.	Coordination number	Coordination mode	Graphical representation of coordination geometry
J	6	<i>fac</i>	
K	5	<i>mer</i>	
L	6	<i>fac</i>	
M	6	<i>fac</i>	

^a The CSD codes are **J**: PAHYAY; **K**: LIVXET; **L**: BZMPSC10; **M**: ILESCO; **N** (see text): JEBTAM or SALCOC, where Cl is the co-ligand.

Structure **J** is the simplest representative of a Co(III)-Salen complex. It bears an ethylene diamine backbone and non-substituted phenolate moieties. Coordination of the homo-bidentate co-ligand 1,2-ethane diol with a small bite angle gives rise to a facial coordination mode. The coordination number is 6. Structure **K** depicts the Salen ligand discussed in the context of this study. In combination with the mono-dentate co-ligand 3,5-difluorophenolate a meridional coordination mode of the Salen donor set is observed. The coordination number is 5.

Structure **L** depicts a Co(III)-Salen complex representative for an aromatic ligand backbone and non-substituted phenolate moieties. In combination with the homo-bidentate co-ligand diphenylacetylacetonate, a facial coordination mode is obtained in the molecular structure. The coordination number is 6.

Structure **M** involves a Salen ligand with an ethylene diamine backbone and non-substituted phenolate moieties. An uncommon substitution is shown on the methylene bridges between the phenolate moieties and the backbone. Coordination of an alpha amino acid as hetero-bidentate co-ligand leads to a facial coordination mode of the Salen donor set. The coordination number is 6.

Structure **N** (not shown) involves Co(III)-Salen complexes in combination with halide (mostly chlorine) ligands giving rise to a meridional coordination mode independently of the substitution mode of the Salen ligand. The coordination number is 5.

Thus, the Salen ligand is much more flexible than anticipated. The coordination geometry is determined by the type of co-ligand (chelating effect), while the substituents on the Salen ligand have no impact on the coordination mode.

A solution of **2** in toluene was heated to 90 °C and pressurised with CO₂ (30 bar). Under these conditions, a set of signals was observed at 1717, 1361 and 1219 cm⁻¹, respectively, resembling closely the result obtained from the reaction of Co(III)-Salen complex **1** with CO₂ (Fig. S2). To test the stability of the carbonate species, the system was cooled to ambient temperature and the pressure decreased in increments to 1 bar. Noteworthy is that the characteristic signals of the phenol-carbonate intermediate were still detected by IR spectroscopy (Fig. S3). Only when the CO₂ atmosphere in the autoclave was released entirely, did the signals disappear (Fig. S4).

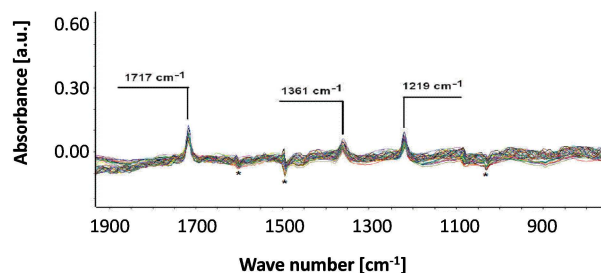


Fig. S2 Difference IR spectra of a solution of **2** in toluene (90 °C) after pressurization with 30 bar CO₂; signals tagged with an asterisk are related to incomplete compensation of the toluene signal.

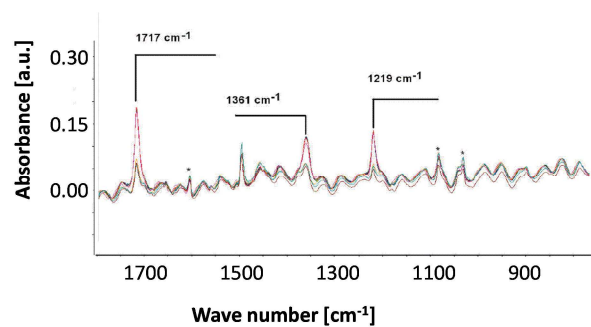


Fig. S3 Difference IR spectra of a solution of **2** in toluene (20 °C) after pressurization with CO₂ and release of the pressure to 1 bar; signals tagged in asterisk are related to incomplete compensation of the toluene signal.

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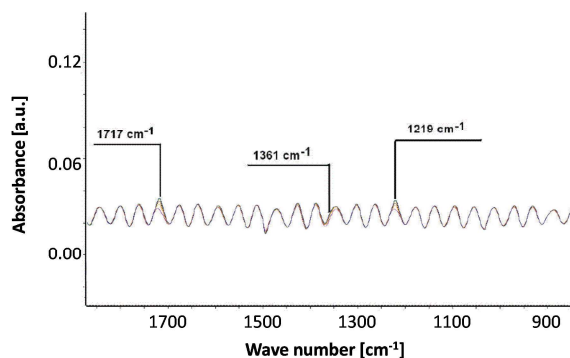


Fig. S4 Difference IR spectra of a solution of **2** in toluene (20 °C) after pressurization with CO₂ and complete removal of CO₂.

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