Carbon Dioxide Fixation: Bifunctional Complexes Containing Acidic and Basic Sites Working as Reversible Carriers[†]

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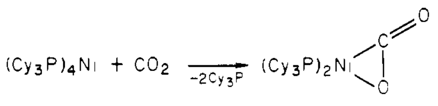
Abstract: Carbon dioxide fixation in its intact form is achieved from "bifunctional" complexes containing in their structure a nucleophilic cobalt(I) and an alkali cation: Co(R-salen)M [R-salen = substituted salen ligand; salen = *N*,*N*'-ethylenebis(salicylideneaminato); M = Li, Na, K, Cs]. The fixation of CO_2 by such systems displays different degrees of reversibility depending on the reaction solvent and the nature of the alkali cation. The X-ray analysis carried out on [Co(*n*-Pr-salen)K-$(CO)_2$(THF)] shows carbon dioxide anchored to the cobalt through a Co–C σ bond, while the oxygens interact with the alkali cation, in a polymeric structure. IR spectra are diagnostic for the presence of CO_2 bonded as a bent molecule in a reduced form displaying three strong bands in the following ranges: 1700–1650, 1300–1250, and 1250–1200 cm^{-1}. The binding of CO_2 is partially prevented in the presence of a crown ether, which can complex the alkali cation. The reaction of [Co(salen)Na(CO_2)] and [Co(salen)Na(THF)] with dicyclohexano-18-crown-6 (DCHC) gave a complex, $[Co(salen)Na]_2$(DCHC), whose structure shows the presence of the intact bifunctional unit where, however, all the coordination sites around the alkali cation are filled by the oxygens from salen and DCHC and are not further available for binding the oxygen atoms of the CO_2 molecule. Crystallographic details for $[Co(n\text{-Pr-salen})K(CO_2)(THF)]_n$, form A, are as follows: space group $C2/c$ (monoclinic); $a = 17.805$ (4) Å, $b = 21.251$ (5) Å, $c = 16.192$ (3) Å; $\beta = 112.50$ (3)°; $Z = 8$; $D_{calcd} = 1.325$ g cm^{-3}. The final R factor was 0.085 for 1096 observed reflections. Crystallographic details for $[Co(n\text{-Pr-salen})K(CO_2)(THF)]_n$, form B, are as follows: space group $C2/c$ (monoclinic); $a = 22.921$ (4) Å, $b = 16.388$ (3) Å, $c = 18.800$ (3) Å; $\beta = 121.74$ (3)°; $Z = 8$; $D_{calcd} = 1.248$ g cm^{-3}. The final R factor was 0.090 for 2287 observed reflections. Crystallographic details for $[Co(salen)Na]_2$(DCHC) are as follows: space group $P2_1/a$ (monoclinic); $a = 14.547$ (3) Å, $b = 16.597$ (4) Å, $c = 14.063$ (3) Å; $\beta = 116.80$ (3)°; $Z = 2$; $D_{calcd} = 1.249$ g cm^{-3}. The final R factor was 0.076 for 682 observed reflections.

Fixation of carbon dioxide in its intact form may represent the first fundamental step for stoichiometric and catalytic "activation" of such a molecule by means of transition-metal complexes.[1] This objective can be achieved provided that fixation of CO_2 by a metallic system leads to a reactive metal–carbon σ bond, while strong metal–oxygen bonds make difficult the transformation of a metal-bonded CO_2. These aspects of transition-metal–carbon dioxide chemistry must be taken into account in a strategy focusing on the metal-assisted CO_2 transfer to organic substrates or its elementary transformations, like those leading to a C–C bond formation. However, any strategy concerning CO_2 activation must take into account the very high thermodynamic stability of this molecule.

As concerns the points above, the general strategies employed for fixing and, subsequently, for activating CO_2 can be summarized:

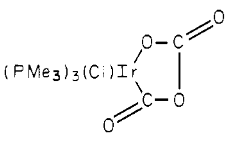
(i) The utilization of highly basic metals: These have various degrees of "oxophilicity" and their utilization takes into account the fact that CO_2 is an oxygen-rich electrophilic molecule.[2]

This approach allowed the exploration of some metal-promoted elementary transformations of CO_2.[3] The fixation of CO_2 by a nickel complex, A, exemplifies such a process:



A

Complexes like A can be considered as intermediates capable of adding a further molecule of CO_2, e.g., to give the head-to-tail dimer of CO_2 bonded to Ir,[5] in the species

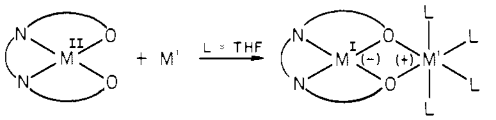


More oxophilic metals like titanium(II) and zirconium(II) promote deoxygenation and disproportionation of CO_2, very probably through its preliminary fixation and heat-to-tail dimerization:[3]

$$4cp_2Ti(CO)_2 + 2\,^{13}CO_2 \rightarrow (cp_2Ti)_4(^{13}CO_3)_2 + 2\,^{13}CO + 8CO$$

(ii) The utilization of bifunctional systems: In many simple reactions carbon dioxide requires for its promotion the presence of acidic–basic systems (bifunctional systems), where the two roles are not played by metal centers. The carboxylation of sodium phenoxide, Grignard reagents, and the catalyzed hydration of CO_2 have been viewed in this light.[6]

Due to the very low availability of bifunctional complexes, this strategy is difficult to pursue. We observed that the reduction of transition-metal complexes containing bicovalent oxygen atoms in their coordination sphere can be generalized as a route leading to the synthesis of "bifunctional complexes"[7]



M' = Li, Na, K. . .; M = Co^{II}; ONNO = salen-type ligand

since the alkali metal reduces the oxidation state of transition metal (M) while remaining bonded to the same ligand as a cation. Therefore we have brought a transition metal in low oxidation state (basic center) and an alkali cation (acidic center) close together within the same complex skeleton.

This report concerns CO_2 fixation by such complexes, the bifunctional nature of which plays the most important role. The

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[†] Dedicated to Professor Lamberto Malatesta on the occasion of his 70th birthday.

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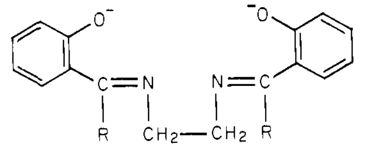
rather unusual bonding mode of a small molecule to be a "bifunctional unit" is fully clarified both structurally and spectroscopically. A preliminary communication reported the data concerning the structure of one of the CO_2 complexes.[8]

Experimental Section

Abbreviations.



R = H, salen = *N,N'*-ethylenebis(salicylideneaminato) dianion; R = Et, Et–salen; R = *n*-Pr, *n*-Pr–salen; THF = tetrahydrofuran; Py = pyridine; and DCHC = dicyclohexano-18-crown-6

Materials. [Co(salen)],[9] [Co(salen)Li(THF)$_{1.5}$],[7] and [Co(salen)Na(THF)][7] were prepared by published procedures. Carbon dioxide was high purity (99.99%) oxygen-free gas.

Physical and Analytical Measurements. Infrared spectra were obtained from Nujol and PTFE (poly(trichlorofluoroethylene)) mulls between KBr plates by using a Perkin-Elmer 283 spectrometer. Nujol and PTFE mulls of CO_2 complexes were prepared in a CO_2 atmosphere. Magnetic measurements were obtained with a Faraday balance.

Conductivity measurements were carried out with a Jones and Joseph bridge (Leeds and Northrup). The thermostatic bath was maintained at 25 ± 0.005 °C and the temperature checked up by an NBS-certified resistance thermometer in connection with a Leeds and Northrup bridge Model C 2. The cell with unplatinized electrodes was calibrated with aqueous KCl solutions, and its constant was found to be 1.06825. The different values of the resistance at 2.5 and 10 kHz were extrapolated to infinite frequency.

General Procedures. Owing to air sensitivity of the complexes, all preparations were carried out under a dry oxygen-free nitrogen or carbon dioxide atmosphere, using standard Schlenk techniques. Solvents were purified and dried by standard methods. Microanalytical determinations of very labile CO_2 complexes are very difficult and not always significant. The best analytical determinations that can be carried out are the measurements of CO_2 absorbed and released.

Quantitative measurements of uptake and release of carbon dioxide were carried out by published procedure and apparatus.[10] The reference method[10] does not require any correction for the absorption of CO_2 by the solvent. An excellent reproducibility of the results was observed.

The gas released by CO_2 complexes was analyzed by gas chromatography and by mass spectrometry, and it was found to be CO_2 only.

The variable solvent content of the complexes described was determined for each preparation by heating the compounds at 150–180 °C in the solid state and analyzing the resulting liquid by GLC.

The absorption of carbon dioxide by a CO_2 carrier compound was carried out by preparing the solution of the appropriate complex under nitrogen. The flask was subsequently evacuated until the solvent started to distill and then filled with CO_2 at atmospheric pressure. Carbon dioxide can be removed from CO_2 complexes suspended in a solvent by partially (in vacuo) distilling the solvent with gentle heating (ca. 30 °C).

All the CO_2 complexes were dried in a stream of carbon dioxide. Detailed procedures are given for the most typical complexes; all the others have been synthesized by similar procedures.

Preparation of [Co(R–salen)] (R = Et, *n*-Pr). The Schiff base Et-salenH_2 (25.0 g, 77.6 mmol), dissolved in 95% ethanol (200 mL), was reacted with an aqueous solution (100 mL) of [$Co(CH_3COO)_2 \cdot 4H_2O$] (18.4 g, 73.9 mmol) under nitrogen. The addition of NaOH (5.15 g, 128.7 mmol) dissolved in 30 mL of water gave a suspension, which was kept stirring for 4 h and then refluxed for 45 min. The resulting red-orange solid was filtered and washed with H_2O (50 mL) and EtOH 95% (50 mL). [Co(Et-Salen)] was recrystallized from THF (400 mL) (yield 53%). Anal. Calcd for [Co(Et–salen)], $C_{20}H_{22}N_2O_2Co$: C, 62.75; H, 5.81; N, 7.23. Found: C, 62.29; H, 5.77; N, 7.35. The synthesis of [Co(*n*-Pr–salen)] was performed following the procedure given above (yield 45%). Anal. Calcd for [Co(*n*-Pr–salen)], $C_{22}H_{26}N_2O_2Co$: C, 64.55; H, 6.36; N, 6.85. Found: C, 63.95; H, 6.45; N, 6.75.

Synthesis of [Co(salen)Cs(THF)$_{0.5}$]. [Co(salen)] (2.65 g, 8.15 mmol) suspended in THF (100 mL) was reacted with cesium metal (1.10 g, 8.27 mmol). The suspension was heated to the melting point of the cesium and then stirred vigorously for 5 h. A deep green color appeared suddenly, and when all the cesium disappeared, a crystalline violet solid formed (2.40 g, 59.6%). Anal. Calcd for Co(salen)Cs(THF)$_{0.5}$, $C_{18}H_{18}N_2O_{2.5}CoCs$: C, 43.72; H, 3.64; N, 5.67. Found: C, 43.11; H, 3.69; N, 5.84. The IR spectrum (Nujol) shows the absence of any C=N band in the 1600–1650-cm^{-1} region.

Synthesis of [Co(*n*-Pr–salen)K(THF)$_{0.5}$]. [Co(*n*-Pr–salen)] (5.20 g, 12.71 mmol) was reduced in THF (200 mL) with potassium metal (0.52 g, 13.3 mmol). The mixture was heated to the potassium melting point and then stirred for 24 h. The resulting deep green solution gave a crystalline compound by addition of Et_2O (200 mL) (3.80 g, 61.2%). Anal. Calcd for [Co(*n*-Pr–salen)K(THF)$_{0.5}$], $C_{24}H_{30}N_2O_{2.5}CoK$: C, 59.50; H, 6.20; N, 5.79. Found: C, 59.54; H, 6.29; N, 5.53.

Preparation of [Co(Et–salen)Li(THF)]. A THF (200 mL) suspension of [Co(Et–salen)] (9.30 g, 24.40 mmol) was reacted with lithium metal (0.18 g, 25.94 mmol). The suspension was stirred overnight. The resulting deep green solution was evaporated to 80 mL and then 100 mL of Et_2O was added. On standing 1 day a crystalline violet solid formed (6.31 g, 56.2%). Anal. Calcd for Co(Et–salen)Li(THF), $C_{24}H_{30}N_2O_3CoLi$: 62.61; H, 6.52; N, 6.09. Found: C, 61.95; H, 6.75; N, 6.15. The IR spectrum does not show any band in the 1600-cm^{-1} region for imino groups.

Reactions with Carbon Dioxide. Reaction of [Co(salen)Li(THF)$_{1.5}$] with Carbon Dioxide. (a) Pyridine Solution. (1) [Co(salen)Li(THF)$_{1.5}$] (0.731 g, 1.67 mmol) dissolved in 25 mL of pyridine adsorbed 12 mL (0.53 mmol) of CO_2 in 8 h at 16 °C, without forming a solid.

(2) The reaction of CO_2 at room temperature with a pyridine (20 mL) solution of [Co(salen)Li(THF)$_{1.5}$] produced only a slight change in the color of the solution, from deep green to green-maroon. By addition of $NaBPh_4$ (1.0 g, 2.92 mmol) a maroon solid precipitated in a few hours; it was shown to be [(Py)Co(salen)Na(CO_2)] (vide infra). The addition of LiCl to a pyridine suspension of [(Py)Co(salen)Na$(CO)_2$] produced a partial loss of CO_2 and a green solution.

(b) Tetrahydrofuran Solution. [Co(salen)Li(THF)$_{1.5}$] (1.596 g, 3.62 mmol), dissolved in 25 mL of THF, absorbed 43.9 mL (1.33 mmol) of CO_2 in 5 h at 23.6 °C, without forming a solid.

(c) Diethyl Ether Solution. [Co(salen)Li(THF)$_{1.5}$] (0.70 g), dissolved in 25 mL of Et_2O, did react with CO_2, giving a gray-green solid. The solid did not dissolve in vacuo. By adding pyridine we observed dissolution of the solid and loss of CO_2.

(d) Toluene Solution. A toluene solution (100 mL) of [Co(salen)Li(THF)$_{1.5}$] (1.45 g, 3.29. mmol) was reacted with CO_2 at room temperature. The reaction produced suddenly a gray-green solid (0.7 g, 56.6%), which did not dissolve in vacuo. Anal. Calcd for [Co(salen)Li(CO_2)], $C_{17}H_{14}N_2O_4LiCo$: C, 54.25; H, 3.72; N, 7.44. Found: C, 54.90; H, 4.40; N, 6.53. The solid reacts with I_2, releasing 0.95 mol of CO_2 per cobalt atom.

Reaction of [Co(salen)Na(THF)] with Carbon Dioxide in THF. (a) Preparation of [Co(salen)Na(CO_2)]. A deep green THF (100 mL) solution of Co(salen)Na(THF) (2.80 g, 6.66 mmol) reacted very rapidly at room temperature and atmospheric pressure with CO_2, giving a maroom microcrystalline solid. The solid was filtered and dried in a stream of CO_2 (2.5 g, 96%). Anal. Calcd for [Co(salen)Na(CO_2)], $C_{17}H_{14}N_2O_4Na$: C, 52.04; H, 3.57; N, 7.14. Found: C, 52.30; H, 4.00; N, 6.82. The solid became deep green in vacuo, losing carbon dioxide. $\chi_M^{corr} = 455.10^{-6}$ cgsu at 293 K. In all experiments CO_2 absorbed was found to be in the range 0.93–0.98 mol per [Co(salen)Na(THF)], i.e., 0.446 g (1.06 mmol) of [Co(salen)Na(THF)] dissolved in 25 mL of THF absorbed 29.75 mL of CO_2 (1.05 mmol) in 15 min at T = 16.3 °C. [Co(salen)Na(CO_2)] was decomposed with dilute H_2SO_4 or THF solutions of I_2. Carbon dioxide measured was always higher than 0.95 mol of CO_2 per cobalt.

(b) Reversible Absorption–Desorption of Carbon Dioxide. [Co(salen)Na(THF)] (1.94 g), dissolved in THF (250 mL), was reacted with CO_2. The reaction led to the quick formation of a maroon solid. By gentle heating at 30 °C in vacuo the mixture lost carbon dioxide, giving back the original deep green solution. The absorption–desorption cycle was repeated 5 times. This required the addition of 30 mL of THF. Then THF was evaporated to 50 mL, and by addition of Et_2O (100 mL), [Co(salen)Na(THF)] was recovered. The recovered [Co(salen)Na(THF)] (0.580 g, 13.8 mmol), dissolved in 25 mL of THF, absorbed in a gas volumetric apparatus 35.8 mL (12.22 mmol) of CO_2 at 17.8 °C. The same reversible absorption–desorption of carbon dioxide was observed starting from [Co(salen)Na(CO_2)].

Reaction of [Co(salen)Na(THF)] with Carbon Dioxide in Pyridine. (a) Preparation of [(Py)Co(salen)Na(CO_2)]. A pyridine (100 mL) solution of Co(salen)Na(THF) (4.30 g, 10.24 mmol) reacted with CO_2 at atmospheric pressure giving a red-maroon microcrystalline solid, which dissolved in vacuo, giving back the starting deep green solution. Upon

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exposure to CO_2 for 10 min, the solid was filtered out and washed with cold Et_2O (25 mL × 2) saturated with CO_2 (3.54 g, 73.4%). In order to eliminate an excess of pyridine in the solid, it must be suspended and washed a few times with cold Et_2O saturated with CO_2. All operations must be carried out in a stream of CO_2. The solid did not lose CO_2 in vacuo. Anal. Calcd for (Py)Co(salen)Na(CO_2), $C_{22}H_{19}N_3O_4NaCo$: C, 56.05; H, 4.03; N, 8.92. Found: C, 55.73; H, 4.55; N, 8.99. The exact content of pyridine and small amounts of Et_2O, which vary from preparation to preparation, can be determined by GLC of the liquid obtained by decomposing the solid at 150–180 °C. The solid was found diamagnetic with a $\chi_M^{corr} = 223.10^{-6}$ cgs units at 293 K. [Co(salen)Na(THF)] (0.760 g, 1.81 mmol), dissolved in 25 mL of pyridine, absorbed 41.7 mL of CO_2 (1.73 mmol) in 25 min at 16.8 °C.

The content of CO_2 was determined by carrying out decomposition of (Py)Co(salen)Na(CO_2) with the follwoing reagents: dilute H_2SO_4, neat $PhCH_2Cl$, pyridine solution of I_2, LiCl; i.e., 0.650 g (1.38 mmol) of the complex gave by the reaction of a concentrated pyridine solution of I_2 28.1 mL (1.17 mmol) of CO_2 at 16.0 °C.

(b) Reversible Absorption–Desorption of Carbon Dioxide. [(Py)Co(salen)Na(CO_2)] (0.55 g) was suspended in 50 mL of pyridine. The mixture lost carbon dioxide and, partially, the solvent (20 mL), giving a deep green solution by heating at 30 °C in vacuo. The final solution absorbed CO_2, giving back the original red-maroon microcrystalline solid. The absorption–desorption cycle was repeated 5 times.

Reaction of [Co(salen)K] with CO_2. Pyridine Solution. [Co(salen)] (3.80 g, 11.69 mmol) was reacted in THF (100 mL) with potassium metal (0.47 g, 12.05 mmol). When the THF mixture was heated up to the boiling point, the potassium melted, and then the suspension was kept on stirring for 12 h. All the potassium disappeared, and a violet solid formed, which was filtered out. When evaporated to dryness, the solution gave a solid, which was dissolved in dry pyridine (50 mL). The pyridine solution reacted with CO_2, producing a microcrystalline maroon solid (1.65 g), which was filtered out, washed with Et_2O saturated with CO_2, and dried in a stream of CO_2. The solid (0.314 g, 0.71 mmol) was decomposed with a pyridine solution of I_2, giving 15.75 mL (0.65 mmol) of CO_2 measured at 16 °C. Anal. Calcd for [(Py)Co(salen)K(CO_2)], $C_{22}H_{19}N_3O_4CoK$: C, 54.20; H, 3.90; N, 8.62. Found: C, 53.70; H, 4.25; N, 7.82. Absorption of CO_2 by [Co(salen)K] gave the same results when carried out in THF solution.

Reaction of [Co(salen)Cs$(THF)_{0.5}$] with Carbon Dioxide. The absorption of CO_2 can be carried out in either THF or Py solution. [Co(salen)Cs$(THF)_{0.5}$] (0.68 g) (1.38 mmol) absorbed 1.31 mmol of CO_2 at 16 °C in 10 mL of pyridine.

A pyridine solution (50 mL) of [Co(salen)Cs$(THF)_{0.5}$] (0.91 g, 1.84 mmol) reacting with CO_2 produced in 24 h a crystalline solid, which was filtered out and washed with Et_2O (0.70 g, 75.8%). Anal. Calcd for $C_{17}H_{14}N_2O_4CsCo$: C, 40.63; H, 2.78; N, 5.57. Found: C, 39.76; H, 2.64; N, 4.12. It was decomposed (0.331 g, 6.59 mmol) with a pyridine solution of I_2, giving 6.05 mmol of CO_2.

Reaction of [Co(Et–salen)Li(THF)] with Carbon Dioxide. A THF (100 mL) solution of Co(Et–salen)Li(THF) (1.72 g, 3.75 mmol) was reacted with CO_2. In a few minutes a deep red microcrystalline solid was obtained, without observing any green color for the solution. The solid was dried in a stream of CO_2 (1.45 g, 82.6%). Anal. Calcd for Co(Et–salen)Li(CO_2)$(THF)_{0.5}$, $C_{23}H_{26}N_2O_{4.5}CoLi$: C, 58.97; H, 5.55; N, 5.98. Found: C, 58.71; H, 5.08; N, 5.92. The complex displays a rather high stability in the solid state, while when suspended in THF, it gives a deep green solution in vacuo.

Preparation of [Co(Et–salen)Na(CO_2)(THF)]. This preparation was performed by following the procedure given above. Anal. Calcd for $C_{25}H_{30}N_2O_6CoNa$: C, 55.97; H, 5.59; N, 5.22. Found: C, 55.82; H, 4.76; N, 6.01.

Synthesis of [Co(*n*-Pr–salen)K(CO_2)(THF)]. Co(*n*-Pr–salen)K$(THF)_{0.5}$ (0.60 g, 1.24 mmol) was dissolved in THF (150 mL) and kept under an atmosphere of CO_2. The solution gave, on standing 5 days, deep red crystals of Co(*n*-Pr–salen)K(CO_2)(THF) (0.5 g, 71.5%). Anal. Calcd for $C_{27}H_{34}N_2O_5CoK$: C, 57.44; H, 6.03; N, 4.96. Found: C, 57.11; H, 6.32; N, 5.22. The corresponding complex containing $^{13}CO_2$ was prepared with generation of $^{13}CO_2$ from $Ba^{13}CO_3$ (95% isotopic purity) and H_2SO_4.

Reaction of [Co(salen)Na(CO_2)] with Dicyclohexano-18-crown-6. A THF (50 mL) solution of [Co(salen)Na(THF)] (1.13 g, 2.68 mmol) was reacted with CO_2. In a few minutes an abundant precipitate of Co(salen)Na(CO_2) was formed, and then a THF (50 mL) solution of dicyclohexano-18-crown-6 (DCHC) (1.10 g, 3.00 mmol) was added in a CO_2 atmosphere. The slow evolution of CO_2 is coupled with the precipitation of a deep green crystalline solid (0.7 g, 46%). The same compound was synthesized by reacting [Co(salen)Na(THF)] and dicyclohexano-18-crown-6 in a THF solution. Anal. Calcd for {$[Co(salen)Na]_2$(DCHC)}·THF, $C_{56}H_{72}N_4O_{11}Co_2Na_2$: C, 58.94; H, 6.31; N, 4.91. Found: C, 58.63; H, 5.65; N, 4.39. The IR spectrum of {$[Co(salen)Na]_2$(DCHC)} is very similar to that of [Co(salen)Na(THF)], showing the disappearance of the C=N bands from the usual 1650–1600 region. $\chi_M^{corr} = 560.10^{-6}$ cgs units at 293 K. The absorption of CO_2 by a THF suspension of [Co(salen)Na(THF)] in the presence of a large excess of DCHC corresponds to 0.65 mol per cobalt.

Conductivity Measurements of [Co(salen)Na(THF)]. A THF (340 mL) solution of [Co(salen)Na(THF)] (0.043 g, 0.102 mmol) 3.01×10^{-3} M prepared under nitrogen was found to have a conductivity at 25 ± 0.005 °C, identical with the specific conductivity of the pure solvent used for preparing the solution, $\chi = 8 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$.

Crystal Data and Intensity Measurements. Co(*n*-Pr–salen)K(CO_2)$(THF)_n$, Form A. A dark red crystal (0.4 × 0.2 × 0.2 mm) sealed in a glass tube capillary was mounted on the goniometric head of a Philips PW1100 four-circle diffractometer equipped with a graphite monochromator and employing Mo radiation. Crystals were found to be monoclinic; the unit-cell parameters were refined by a least-squares method to give the best fit between calculated and observed settings, χ, ϕ, and 2θ measured at 20 °C for 25 reflections. The results are as follows: a = 17.805 (4) Å, b = 21.251 (5) Å, c = 16.192 (3) Å, β = 112.50 (3)°. From systematic absences the space group is either *Cc* or *C*2/*c*; further investigation confirmed the latter one. The calculated density for eight molecules in the cell is 1.325 g cm^{-3}. The linear absorption coefficient μ(Mo Kα) has the value 8.12 cm^{-1}. Intensities were measured by the ω–2θ scan technique within a sphere of radious $2\theta \leq 50°$. Each reflection was measured with a scan width of 1.2°, a scan speed of 0.06° s^{-1}, and two background measurements for 10 s on each side of the reflection. Three reflections were monitored after every 180 min, and no apparent decay in intensities was detected. A unique data set of 4878 reflections was collected, of which 3782 were too weak to be measured $[I \leq 3\sigma(I)]$[11] and were considered as "unobserved". Intensities data were corrected for Lorentz and polarization effects. No absorption correction was applied.

[Co(*n*-Pr–salen)K(CO_2)(THF)]$_n$, Form B. A dark red crystal (0.5 × 0.3 × 0.3 mm) sealed in a capillary was employed for the collection of intensity data by using the same measurement procedure already described for the form A and led to the following results: crystals are monoclinic, space group *Cc* or *C*2/*c*, the latter confirmed by the structural analysis. The lattice constants are as follows: a = 22.921 (4) Å, b = 16.388 (3) Å, c = 18.800 (3) Å, b = 121.74 (3)°. Assuming a cell content of 8($C_{27}H_{34}N_2O_5CoK$), the calculated density is D_{calcd} = 1.248 g cm^{-3}, and the linear absorption coefficient is μ(Mo Kα) = 7.65 cm^{-1}. A number of 4980 independent reflections were collected out to $2\theta = 50°$; 2287 of these had $I \geq 3\sigma(I)$[11] and were retained for subsequent computations. During data collection, the crystal was severely damaged, as displayed by the progressive decay of the intensity of the three monitor reflections. The fall in intensity reached 30% at the end of data collection. A correction for this crystal deterioration was then applied to scale the intensity data to a common level.[12] Usual Lorentz–polarization factors were applied. With the deterioration of the crystal and the poor quality of the data taken into account, absorption effects were deemed unimportant and were therefore neglected.

$[Co(salen)Na]_2$(DCHC). After some preliminary rotation and Weissenberg photographs, a well-formed black crystal with dimensions 0.18 × 0.18 × 0.22 mm sealed in a glass capillary under nitrogen was examined. The crystal was found to be monoclinic, space group $P2_1/a$ from systematic extinctions. Cell dimensions as determined by least-squares fitting of the angular θ, χ, and ϕ values of 25 reflections are (at 17 °C) as follows: a = 14.547 (3) Å, b = 16.597 (4) Å, c = 14.063 (3) Å, β = 116.80 (3)°. For a cell content of two formula units, D_{calcd} = 1.249 g cm^{-3}. The intensity data were measured with the ω–2θ scan technique up to $\theta = 20°$. Beyond this limit no reliable intensities were recorded because of the low diffracting power of the crystal. The scan speed was 0.02° s^{-1}, the scan width 1.4°. As a general check on experimental stability, the intensities of three reflections were monitored every 180 min. These did not vary to any significant degree during the entire period of data collection. The intensities were corrected for Lorentz and polarization factors but not for absorption (μ = 5.9 cm^{-1} for Mo Kα). A total of 2803 independent reflections was measured; of these, 2121 having $I \leq 2.5\sigma(I)$[11] were considered as "unobserved".

Structure Solution and Refinement. [Co(*n*-Pr–salen)K(CO_2)(THF)]$_n$, Form A. The structure was solved by direct methods (MULTAN76).[13] The

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[11] Standard deviations on intensity were computed as $I = [P + 0.25 \cdot (T_p/T_B)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$, where P is the total peak count in a scan of time T_p, B_1 and B_2 are the background counts each in a time T_B, and I is the intensity equal to $[P - 0.5(T_p/T_B)(B_1 + B_2)]$.

[12] The correction for the intensity decay was carried out by linear interpolation for groups of reflections taken in the range t_i–$(t_i + \Delta t_i)$, where Δt_i is the time between two successive measurements of the monitor reflections, i.e., 180 min.

E map computed with the 200 largest E's with signs from the set having the highest figure of merit revealed the positions of Co and K atoms in the asymmetric unit. The structure was completed by successive Fourier syntheses and refined by full-matrix least-squares methods.[14] Owing to the large value of the parameters to observations ratio, thermal parameters were refined anisotropically only for non-carbon atoms, with the exception of the oxygen of the tetrahydrofuran group. Carbon atoms of the propylic chains of Co(Pr–salen) showed relatively high apparent thermal motion, probably indicative of positional disorder. All atoms of the tetrahydrofuran group have very high thermal parameters; this was ascribed to statistical site occupancy. Some least-squares cycles were carried out with reduced occupancy parameters: results seem to indicate that thermal parameters assume reasonable values when the occupancy of the tetrahydrofuran group is about 50%. Therefore the positions of atoms of the propylic chains and of THF groups are defined only with large approximation, as shown by quite unrealistic bond lengths and angles. Nevertheless, previous refinement was considered complete in connection with the poorness of data and the bad quality of the crystal. However, the results are adequate to reveal all main structural features of chemical interest. The final R value was 0.085 for the 1096 observed reflections: R_w[15] was 0.101.

[Co(n-Pr–salen)K(CO_2)(THF)]$_n$, Form B. The structure was solved by the same method as that used for the A form. The anisotropic refinement was carried out by full-matrix least-squares methods. In the last cycles the contribution of hydrogen atoms at fixed positions (1.08 Å from the carbon atoms to which they are bonded) was considered (with the exception of the methyl groups of propylic chains). To these hydrogen atoms an isotropic thermal parameter equal to 6 $Å^2$ was assigned. A table of hydrogen atom positions is available as supplementary material. The final R value is 0.090; R_w[15] was 0.129.

[Co(salen)Na]$_2$(DCHC). The structure was solved by direct methods and Fourier techniques with SHELX-76[16] and refined by full-matrix least-squares methods.[17] Because of the unfavorable observations-to-parameters ratio, anisotropic thermal parameters were refined only for cobalt and sodium atoms. Furthermore, the phenyl rings of the Co–salen group were constrained to perfect hexagons with a C–C distance of 1.395 Å and refined with their H atoms as rigid groups. In the last cycles of refinement, the contribution of hydrogen atoms at the computed positions with a constrained distance of 1.08 Å from C atoms was included. To all the H atoms a common isotropic thermal parameter was assigned; this value refined to $U = 0.12$ $Å^2$. When the R index was 0.10, a difference Fourier showed some maxima that were assigned to a molecule of tetrahydrofuran used as solvent of crystallization. To this THF molecule was assigned a reduced occupancy of 0.5, and the single atomic positions were refined, constraining C–O and C–C distances to 1.39 and 1.50 Å (∓0.05 Å), respectively. A common thermal parameter for these atoms refined to the value $U = 0.13$ $Å^2$. The refinement was stopped when all shift/estimated standard deviation ratios were less than 0.1. The R value converged to 0.076 for 682 reflections and 144 parameters; R_w[15] was 0.079.

The scattering factors for Co, K, O, C, and H atoms of form A and B were taken from International Tables for X-ray Crystallography.[18] The scattering factors of Co, O, N, C, and H atoms of complex V were those of SHELX system for programs; Na scattering factor was taken from ref 18. To the form factors a correction for anomalous dispersion was applied.[19] Atomic coordinates and thermal parameters are presented in Tables I–III.

The list of observed and calculated structure factors for the three compounds, the tables of computed hydrogen coordinates for form B and complex V, as well as the complete information concerning all interatomic distances and angles for the three compounds, are available as supplementary material.

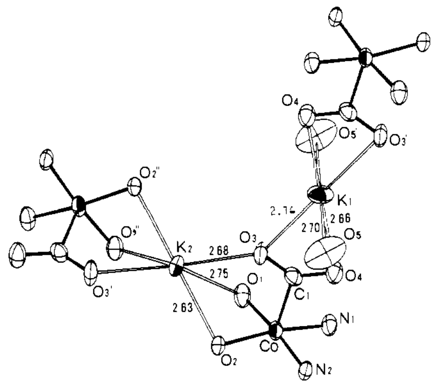


Figure 1. View of the repetitive unit present in Co(n-Pr–salen)K(CO_2)(THF), form B.

Results and Discussion

Deep green solutions of bimetallic complexes [Co(R–salen)M] ([Co(R–salen)M] exemplifies a bimetallic cobalt(I)–alkali cation complex; R–salen is a substituted salen ligand [salen= N,N'-ethylenebis(salicylideneaminato) dianion]; M = alkali cation) in solvents like tetrahydrofuran (THF), pyridine (Py), or toluene absorb 1 mol of carbon dioxide per bimetallic unit at room temperature and atmospheric pressure:

$$\underset{\text{I}}{\text{Co(R–salen)ML}_n} + \text{CO}_2 \rightleftarrows \underset{\text{II}}{\text{Co(R–salen)MCO}_2\text{L}_n} \qquad (1)$$

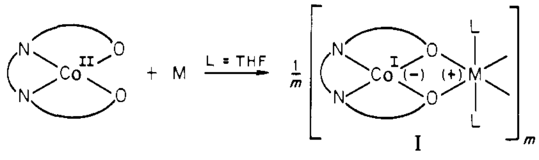
M = Li, Na, K, Cs; R–salen =
salen, Et–salen, n-Pr–salen; L = THF, Py

The absorption of CO_2 is reversible: the complexes II precipitate from the solution as red-maroon solids, which dissolve in vacuo, giving back the original deep green solutions.

This report will mainly concern the factors affecting the occurrence of reaction 1 as well as the "status" of CO_2 bonded in complexes II.

In order to understand the rather unique property of the metal complexes I in binding to carbon dioxide, we must refer to their genesis and their structure either in the solid state or in solution.

Reduction of Co(R–salen) complexes performed with alkali metals achieved both goals: to form a nucleophilic cobalt(I) and to produce an alkali cation that remains complexed within the same structure:



(2)

M = Li, Na, K, Cs; O N N O = R-salen ligand

This is the direct consequence of the presence of a set of bicovalent oxygen atoms on the polydentate ligand surrounding the transition metal.[7,20] The solid-state structure of complexes I[7] determined for Co(salen)Li$(THF)_{1.5}$ and [Co(salen)Na(THF)]$_n$ can be strictly related to their nature in solution, where they maintain their bimetallic nature.

The presence of the neutral intact ion-pair unit in solution is strongly supported by the finding that a THF solution of Co(salen)Na(THF) has the same conductivity as the neat THF (see Experimental Section). The change from solid state to solution for complexes I is probably restricted to the change in molecular

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(13) Main, P.; Woolfson, M. M.; Lessinger, L.; Germain, G.; Declerq, J. P. MULTAN76, a system of computer programs for the automatic solution of crystal structures for X-ray diffraction data, University of York, York, England, and University of Louvain-La-Neuve, Louvian, Belgium, 1976.

(14) The program used in the calculations was a locally adapted version of ORFLS (Busing, W. R.; Martin, K. O.; Levy, H. A. ORFLS, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1962). The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w is $4F_o^2/\sigma(F_o^2)$. After the last cycle the quantity $s = [\sum(w\Delta F_o^2)/(m - n)]^{1/2}$ was 2.76 and 3.62 for form A and B, respectively.

(15) R index is defined as $\sum(|F_o| - |F_c|)/\sum|F_o|$ and R_w as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]$.

(16) Sheldrick, G. M. SHELX-76, a program for crystal structure determination. University of Cambridge, Cambridge, England, 1976.

(17) The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w is $1/(\sigma^2(F) + aF^2)$; a was refined in the last cycle to 0.00262. The rms deviation of a reflection of unit weight on the absolute scale of F_c was 5.06.

(18) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

(19) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(20) Floriani, C.; Calderazzo, F.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* **1973**, *384*–385. Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L.; Zotti, E.; Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2310–2316. Pasquali, M.; Marchetti, F.; Floriani, C.; Cesari, M. *Inorg. Chem.* **1980**, *19*, 1198–2001.

Table I. Fractional Atomic Coordinates and Thermal Parameters of [Co(n-Pr-salen)K(CO_2)THF] (Form A)

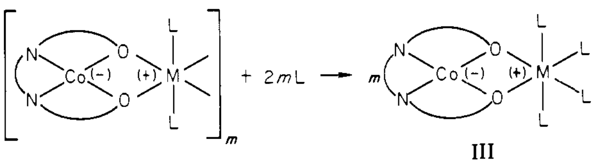
atom	x	y	z	U or U_{eq},[a] Å^2
Co	0.8389 (2)	−0.1739 (2)	0.5467 (2)	0.063
K(1)	0.0	0.0	0.50	0.146
K(2)	0.0	−0.1419 (4)	0.75	0.078
O(1)	0.9274 (9)	−0.2243 (7)	0.6154 (9)	0.075
O(2)	0.8391 (8)	−0.1482 (6)	0.6552 (10)	0.072
O(3)	0.9621 (9)	−0.0909 (8)	0.5929 (10)	0.100
O(4)	0.8665 (10)	−0.0759 (9)	0.4535 (13)	0.121
O(5)	−0.0922 (30)	0.0808 (24)	0.5372 (32)	0.337 (21)
N(1)	0.8349 (11)	−0.2136 (9)	0.4438 (12)	0.077
N(2)	0.7369 (10)	−0.1337 (8)	0.4832 (11)	0.063
C(1)	0.9005 (17)	−0.1019 (13)	0.5252 (21)	0.077 (9)
C(2)	0.9709 (15)	−0.2575 (12)	0.5827 (18)	0.070 (7)
C(3)	1.0450 (16)	−0.2844 (12)	0.6496 (17)	0.098 (9)
C(4)	1.0957 (15)	−0.3205 (14)	0.6280 (18)	0.105 (9)
C(5)	1.0818 (17)	−0.3366 (13)	0.5399 (19)	0.113 (10)
C(6)	1.0101 (17)	−0.3112 (13)	0.4725 (18)	0.109 (10)
C(7)	0.9516 (15)	−0.2721 (12)	0.4957 (18)	0.085 (7)
C(8)	0.8802 (18)	−0.2529 (14)	0.4188 (19)	0.103 (10)
C(9)	0.7603 (17)	−0.1889 (13)	0.3628 (18)	0.110 (10)
C(10)	0.7058 (15)	−0.1574 (12)	0.3940 (18)	0.091 (9)
C(11)	0.6970 (15)	−0.0976 (12)	0.5194 (18)	0.079 (7)
C(12)	0.7300 (13)	−0.0736 (10)	0.6066 (15)	0.054 (6)
C(13)	0.6925 (15)	−0.0257 (12)	0.6279 (18)	0.089 (9)
C(14)	0.7210 (19)	−0.0028 (15)	0.7141 (23)	0.129 (10)
C(15)	0.7866 (18)	−0.0305 (14)	0.7866 (20)	0.120 (10)
C(16)	0.8243 (14)	−0.0808 (12)	0.7597 (17)	0.089 (7)
C(17)	0.7967 (14)	−0.1030 (12)	0.6722 (16)	0.060 (6)
C(18)	0.8420 (18)	−0.3007 (15)	0.3201 (21)	0.137 (11)
C(19)	0.8827 (19)	−0.2504 (16)	0.2957 (22)	0.146 (11)
C(20)	0.8498 (26)	−0.3073 (20)	0.2000 (29)	0.233 (19)
C(21)	0.6087 (14)	−0.0737 (11)	0.4561 (16)	0.090 (7)
C(22)	0.6202 (17)	−0.0121 (13)	0.4038 (18)	0.113 (10)
C(23)	0.5238 (28)	0.0153 (23)	0.3712 (31)	0.160 (21)
C(24)	−0.0805 (42)	0.0699 (28)	0.6455 (45)	0.360 (29)
C(25)	−0.1593 (42)	0.0853 (34)	0.5953 (43)	0.250 (30)
C(26)	−0.1724 (60)	0.1473 (42)	0.5429 (59)	0.413 (49)
C(27)	−0.0752 (44)	0.1448 (37)	0.5458 (43)	0.304 (33)

Thermal Parameters for Anisotropically Refined Atoms[b]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.052 (1)	0.064 (2)	0.069 (2)	−0.011 (2)	0.017 (1)	0.002 (3)
K(1)	0.118 (8)	0.091 (7)	−0.269 (11)	−0.014 (7)	0.117 (9)	0.050 (8)
K(2)	0.053 (5)	0.091 (7)	0.075 (6)		0.005 (5)	
O(1)	0.079 (12)	0.066 (11)	0.060 (11)	0.009 (11)	0.008 (9)	−0.006 (10)
O(2)	0.044 (9)	0.069 (11)	0.086 (12)	0.005 (9)	0.008 (9)	0.005 (8)
O(3)	0.066 (12)	0.117 (16)	0.082 (12)	−0.039 (11)	−0.011 (10)	0.035 (11)
O(4)	0.082 (12)	0.155 (18)	0.119 (16)	−0.023 (12)	0.030 (12)	0.068 (14)
N(1)	0.063 (14)	0.085 (16)	0.063 (15)	0.014 (12)	0.001 (11)	0.006 (13)
N(2)	0.062 (14)	0.073 (16)	0.050 (12)	−0.016 (16)	0.014 (10)	−0.008 (11)

[a] U_{eq} are the equivalent isotropic temperature factors according to Hamilton.[27] [b] In the form: $\exp(-2\pi^2(\Sigma_i\Sigma_j h_i h_j a_i{}^* a_j{}^* U_{ij}))$.

complexity as a consequence of the increased solvation of the alkali cation,[7] as shown in reaction 3:



(3)

III

For an explaination of the essential role played by the acidic–basic Co–M unit in binding carbon dioxide, the structure of one of these CO_2 carriers, [Co(n-Pr-salen)K(CO_2)(THF)]$_n$, is the most appropriate starting point.

The crystals of [Co(n-Pr-salen)K(CO_2)(THF)]$_n$ are dimorphous, and the X-ray analysis was carried out on both forms. The structural parameters are very close for both forms, as reported in Tables IV and V. Because of the poor quality of form A crystals, our discussions will be restricted to form B. The CO_2 complex has a polymeric structure whose repetitive unit is given in Figure 1, while Figure 2 shows the details concerning the coordination sphere of the cobalt and the Co(n-Pr–salen)CO_2 unit is drawn in Figure 3. The most important result from this structure is associated with the anchoring mode of the CO_2, which binds cobalt through the carbon, while both oxygens interact with alkali cations. Therefore both metals centers are involved in binding CO_2. Cobalt is in a pseudo-square-planar coordination determined by the tetradentate n-Pr–salen ligand with the fifth

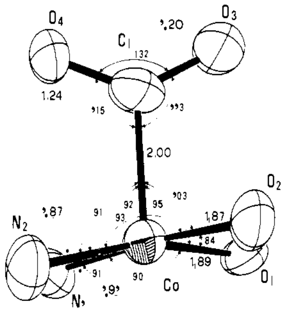


Figure 2. Coordination sphere around cobalt in Co(n-Pr–salen)K(CO_2)(THF), form B, with the most relevant bond distances (Å) and angles (deg).

Table II. Fractional Atomic Coordinates and Thermal Parameters[a] for Non-Hydrogen Atoms of [Co(n-Pr–salen)K(CO_2)(THF)] (Form B)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.8552 (1)	0.1817 (1)	0.5548 (1)	0.058 (2)	0.065 (1)	0.030 (1)	0.026 (2)	0.020 (2)	0.007 (1)
K(1)	0.0	0.0	0.50	0.069 (4)	0.082 (4)	0.109 (4)	0.013 (3)	0.055 (3)	−0.020 (4)
K(2)	0.0	0.1359 (3)	0.75	0.052 (4)	0.073 (4)	0.033 (3)		0.011 (2)	
O(1)	0.9286 (6)	0.2510 (6)	0.6277 (6)	0.087 (8)	0.048 (7)	0.043 (6)	0.002 (6)	0.033 (6)	−0.001 (5)
O(2)	0.8656 (5)	0.1400 (6)	0.6537 (5)	0.052 (6)	0.069 (7)	0.035 (5)	0.006 (6)	0.022 (5)	0.017 (5)
O(3)	0.9624 (6)	0.0818 (7)	0.5971 (6)	0.075 (8)	0.110 (9)	0.029 (5)	0.053 (6)	0.016 (6)	0.005 (5)
O(4)	0.8917 (6)	0.0935 (7)	0.4588 (6)	0.081 (8)	0.111 (9)	0.048 (6)	0.049 (8)	0.032 (6)	0.000 (7)
O(5)	0.9084 (8)	−0.1182 (10)	0.4719 (11)	0.116 (11)	0.080 (11)	0.244 (17)	0.002 (10)	0.115 (13)	−0.029 (11)
N(1)	0.8352 (7)	0.2495 (9)	0.4618 (7)	0.067 (10)	0.079 (11)	0.033 (8)	0.042 (8)	0.022 (8)	0.013 (7)
N(2)	0.7770 (6)	0.1182 (9)	0.4873 (7)	0.050 (8)	0.095 (12)	0.030 (6)	0.023 (8)	0.013 (6)	0.004 (7)
C(1)	0.9130 (8)	0.1063 (9)	0.5339 (10)	0.071 (11)	0.057 (11)	0.058 (10)	0.018 (10)	0.044 (9)	−0.003 (9)
C(2)	0.9645 (10)	0.2978 (9)	0.6077 (10)	0.111 (15)	0.031 (11)	0.061 (13)	0.024 (10)	0.055 (13)	0.009 (9)
C(3)	1.0302 (10)	0.3237 (11)	0.6746 (11)	0.092 (11)	0.059 (11)	0.067 (11)	−0.016 (11)	0.038 (11)	−0.001 (11)
C(4)	1.0695 (10)	0.3722 (11)	0.6575 (11)	0.110 (17)	0.077 (14)	0.078 (14)	−0.013 (13)	0.051 (14)	0.016 (11)
C(5)	1.0443 (14)	0.4011 (13)	0.5762 (17)	0.139 (21)	0.073 (15)	0.145 (22)	0.023 (16)	0.103 (19)	0.029 (17)
C(6)	0.9816 (13)	0.3767 (12)	0.5106 (14)	0.108 (17)	0.065 (12)	0.101 (18)	0.015 (13)	0.074 (16)	0.030 (11)
C(7)	0.9400 (10)	0.3254 (11)	0.5242 (10)	0.085 (13)	0.057 (11)	0.060 (10)	0.029 (11)	0.039 (11)	0.011 (9)
C(8)	0.8725 (12)	0.3058 (13)	0.4563 (12)	0.116 (15)	0.076 (14)	0.079 (14)	0.055 (13)	0.074 (19)	0.029 (11)
C(9)	0.7664 (11)	0.2307 (15)	0.3924 (12)	0.083 (13)	0.117 (18)	0.067 (13)	0.045 (13)	0.035 (11)	0.019 (11)
C(10)	0.7459 (9)	0.1415 (17)	0.3976 (10)	0.056 (11)	0.189 (23)	0.027 (8)	0.031 (15)	0.005 (8)	0.000 (11)
C(11)	0.7540 (9)	0.0563 (13)	0.5048 (10)	0.048 (11)	0.107 (22)	0.035 (10)	−0.002 (11)	0.009 (8)	−0.015 (11)
C(12)	0.7785 (9)	0.0331 (12)	0.5892 (11)	0.052 (11)	0.097 (15)	0.058 (11)	−0.021 (11)	0.013 (9)	−0.007 (11)
C(13)	0.7509 (10)	−0.0301 (15)	0.6076 (13)	0.069 (13)	0.129 (18)	0.062 (14)	−0.026 (13)	0.000 (11)	0.007 (13)
C(14)	0.7681 (12)	−0.0535 (14)	0.6886 (17)	0.089 (17)	0.099 (18)	0.152 (19)	−0.024 (15)	0.047 (16)	0.017 (17)
C(15)	0.8203 (10)	−0.0039 (15)	0.7605 (12)	0.073 (13)	0.141 (19)	0.074 (14)	−0.019 (13)	0.028 (11)	0.035 (13)
C(16)	0.8502 (8)	0.0589 (12)	0.7449 (9)	0.056 (11)	0.110 (15)	0.037 (9)	−0.006 (10)	0.022 (8)	0.011 (9)
C(17)	0.8313 (8)	0.0799 (11)	0.6586 (9)	0.044 (10)	0.082 (14)	0.052 (10)	0.027 (10)	0.016 (9)	0.008 (9)
C(18)	0.8429 (10)	0.3529 (11)	0.3736 (11)	0.127 (17)	0.097 (15)	0.075 (11)	0.060 (15)	0.068 (13)	0.049 (11)
C(19)	0.8605 (10)	0.3106 (16)	0.3164 (11)	0.096 (17)	0.210 (26)	0.075 (13)	0.021 (19)	0.057 (13)	0.052 (17)
C(20)	0.8279 (18)	0.3732 (27)	0.2413 (18)	0.241 (37)	0.449 (53)	0.128 (22)	0.131 (39)	0.111 (24)	0.181 (29)
C(21)	0.6972 (10)	−0.0008 (13)	0.4370 (11)	0.075 (11)	0.114 (16)	0.082 (13)	0.011 (11)	0.039 (11)	−0.004 (11)
C(22)	0.6290 (11)	0.0284 (16)	0.4202 (11)	0.081 (13)	0.185 (24)	0.067 (13)	0.053 (15)	0.024 (11)	0.011 (13)
C(23)	0.5728 (11)	−0.0384 (18)	0.3614 (15)	0.073 (15)	0.196 (27)	0.132 (21)	−0.023 (18)	−0.008 (19)	−0.072 (20)
C(24)	0.9144 (16)	−0.1953 (17)	0.4574 (20)	0.200 (33)	0.065 (19)	0.276 (47)	0.004 (19)	0.163 (35)	0.000 (21)
C(25)	0.8635 (22)	−0.2373 (17)	0.4641 (31)	0.273 (40)	0.057 (19)	0.425 (65)	−0.044 (23)	0.172 (46)	−0.061 (26)
C(26)	0.8275 (15)	−0.1814 (25)	0.4908 (19)	0.139 (23)	0.166 (26)	0.174 (30)	0.019 (24)	0.062 (22)	−0.023 (25)
C(27)	0.8515 (14)	−0.1062 (17)	0.4783 (22)	0.116 (21)	0.079 (19)	0.297 (43)	−0.006 (16)	0.111 (25)	−0.017 (21)

[a] Estimated standard deviations in parentheses refer to the last digit. The form of the anisotropic thermal parameters is $\exp[-2\pi^2(\Sigma_i\Sigma_j h_i h_j a_i{}^* a_j{}^* U_{ij})]$.

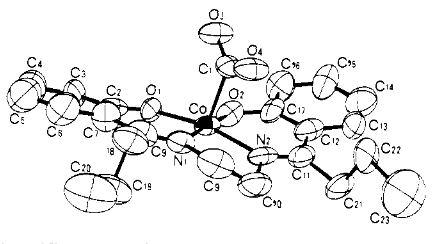
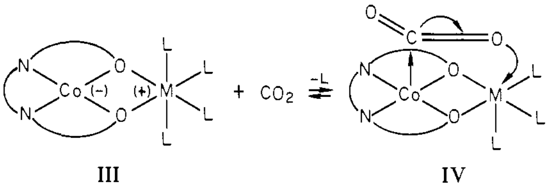


Figure 3. Simplified view of the Co(n-Pr–salen)(CO_2)] unit in complex Co(n-Pr–salen)K(CO_2)(THF), form B.

position occupied by the carbon atom of CO_2. Six oxygens from THF, salen, and CO_2 determine a pseudooctahedral cavity for K^+. Disregarding all the structural parameters concerning the Co(n-Pr–salen) unit that fall in the usual range,[21] the most important ones are related to the Co–CO_2–K unit (Figure 2): the Co–C bond distance approximates to a metal–carbon σ bond [2.00 (1) Å] with some carbene character, to be compared with Co–C σ bonds as reported in R–Co(salen) complexes;[21,22] a significant reduction of the C–O bond order [1.20 (2) and 1.24 (2) Å] agrees with the IR spectrum showing C–O stretching frequencies in the 1600–1700- and 1200–1300-cm^{-1} regions Table VII.

This structure emphasized the role played by both metal centers in binding CO_2. Therefore the peculiar property of complexes I, which reversibly fix CO_2, is due mainly to their bifunctional nature.

As a consequence of this, the fixation of CO_2 by complexes I can be depicted as resulting from a "concerted" attack by the nucleophilic cobalt(I) on the electrophilic carbon, while the basic oxygens interact with the Lewis acid center. The difference between the solid-state structure of [Co(n-Pr–salen)K(CO_2)(THF)] and that proposed in IV is expected when we pass from

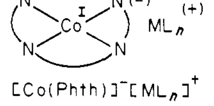


(4)

III IV

solution to the solid state, since the labile solvation sphere around M^+ is lost and the molecular complexity increases through polymerization.

This is the reason for the very low solubility of CO_2 complexes II. Other information can be cited to support the possible role of a bifunctional acid–base unit in binding CO_2. It was recently reported that phthalocyaninatocobalt(I),[23]



$[Co(Phth)]^-[ML_n]^+$

M = Li, L = THF

although containing a strong nucleophile, does not react with

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[21] Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385–403.

[22] Calligaris, M.; Minichelli, D.; Nardin, G.; Randaccio, L. *J. Chem. Soc. A* **1971**, 2720–2724. Cesari, M.; Neri, C.; Perego, G.; Perrotti, E.; Zazzetta, A. *J. Chem. Soc., Chem. Commun.* **1970**, 276–277.

[23] Eckert, H., Schier, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 794–795.

Table III. Fractional Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms of Complex V[a]

atom	x/a	y/b	z/c	U Å^2
		Co(salen) Group		
Co	0.8217 (4)	0.4940 (3)	0.6613 (4)	*b*
O(1)	0.7585 (15)	0.4449 (12)	0.7373 (17)	0.056 (7)
O(2)	0.7441 (14)	0.4183 (11)	0.5523 (15)	0.043 (6)
N(1)	0.8941 (20)	0.5618 (16)	0.7646 (23)	0.062 (9)
N(2)	0.8790 (20)	0.5428 (16)	0.5878 (22)	0.064 (9)
C(1)	0.7746 (15)	0.4602 (12)	0.8347 (19)	0.047 (10)
C(2)	0.7182 (15)	0.4154 (12)	0.8741 (19)	0.054 (10)
C(3)	0.7288 (15)	0.4306 (12)	0.9762 (19)	0.097 (13)
C(4)	0.7960 (15)	0.4907 (12)	1.0387 (19)	0.108 (14)
C(5)	0.8525 (15)	0.5354 (12)	0.9993 (19)	0.083 (14)
C(6)	0.8418 (15)	0.5202 (12)	0.8972 (19)	0.065 (11)
C(7)	0.8979 (25)	0.5662 (22)	0.8544 (28)	0.073 (12)
C(8)	0.9729 (27)	0.6124 (21)	0.7527 (28)	0.076 (12)
C(9)	0.9334 (25)	0.6229 (19)	0.6337 (26)	0.061 (11)
C(10)	0.8711 (22)	0.5213 (19)	0.4916 (25)	0.062 (11)
C(11)	0.8142 (14)	0.4553 (10)	0.4255 (17)	0.059 (10)
C(12)	0.8176 (14)	0.4378 (10)	0.3302 (17)	0.062 (11)
C(13)	0.7669 (14)	0.3700 (10)	0.2713 (17)	0.042 (9)
C(14)	0.7127 (14)	0.3197 (10)	0.3077 (17)	0.059 (11)
C(15)	0.7092 (14)	0.3372 (10)	0.4031 (17)	0.047 (10)
C(16)	0.7599 (14)	0.4050 (10)	0.4620 (17)	0.047 (10)
		Sodium Dicyclohexyl-18-crown-6 Ether		
Na	0.6053 (9)	0.4186 (7)	0.5840 (10)	*b*
O(3)	0.5176 (18)	0.5384 (14)	0.6268 (18)	0.071 (7)
O(4)	0.4771 (14)	0.3738 (12)	0.6450 (14)	0.042 (6)
O(5)	0.5019 (17)	0.3077 (13)	0.4747 (17)	0.060 (7)
C(17)	0.4790 (23)	0.5079 (22)	0.6947 (24)	0.072 (10)
C(18)	0.4087 (25)	0.4394 (19)	0.6491 (25)	0.065 (11)
C(19)	0.4162 (24)	0.3016 (19)	0.5911 (25)	0.054 (10)
C(20)	0.4740 (23)	0.2563 (19)	0.5401 (25)	0.053 (10)
C(21)	0.5781 (22)	0.2228 (19)	0.6324 (24)	0.057 (11)
C(22)	0.5554 (24)	0.1662 (17)	0.7065 (25)	0.053 (11)
C(23)	0.4933 (25)	0.2100 (21)	0.7504 (28)	0.074 (12)
C(24)	0.3989 (27)	0.2474 (20)	0.6696 (28)	0.078 (12)
C(25)	0.4107 (36)	0.3348 (28)	0.3853 (39)	0.136 (20)
C(26)	0.4122 (35)	0.4010 (27)	0.3300 (38)	0.136 (19)
		Tetrahydrofuran		
O(6)	0.3396 (42)	0.3065 (34)	−0.0953 (42)	0.127 (14)
C(27)	0.3514 (54)	0.2693 (42)	−0.0051 (58)	
C(28)	0.4323 (57)	0.3124 (46)	0.0841 (45)	
C(29)	0.4852 (46)	0.3536 (45)	0.0300 (55)	
C(30)	0.4077 (56)	0.3694 (44)	−0.0783 (50)	

Anisotropic Temperature Factors of Co and Na in the Form $\exp(-2\pi^2(\Sigma h_i^2 a^*{}_i^2 U_{ii} 2\Sigma h_i h_j a^*{}_i a^*{}_j U_{ij}))$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.043 (3)	0.041 (3)	0.053 (3)	−0.003 (3)	0.019 (2)	0.003 (4)
Na	0.047 (9)	0.042 (9)	0.066 (10)	−0.010 (7)	0.024 (8)	−0.006 (8)

[a] Estimated standard deviations in parentheses refer to the last digit.

carbon dioxide or other CO_2-like molecules. This may be explained by the fact that the action of cobalt(I) nucleophile is not associated with a Lewis acid held by the same structure.

A further support for this hypothesis comes from the reaction

$$2[\mathrm{Co(salen)Na(CO_2)}] + \underset{\mathrm{DCHC}}{C_{20}H_{36}O_6} \xrightarrow[-2CO_2]{} \underset{\mathrm{V}}{[\mathrm{Co(salen)Na}]_2(\mathrm{DCHC})} \quad (5)$$

DCHC = dicyclohexano-18-crown-6

Dicyclohexano-18-crown-6 ($C_{20}H_{36}O_6$) caused the partial loss of CO_2 from Co(salen)Na$(CO)_2$ in THF even in a CO_2 atmosphere, and as expected, Co(salen)Na(THF) reacts only in a limited extent with CO_2 in a THF solution containing the crown ether, where it formed complex V. Complex V is practically diamagnetic ($\chi_M^{corr} = 560.10^{-6}$ cgs units at 293 K), as expected for a square-planar d^8 cobalt(I), while the IR spectrum shows the absence of any C=N band as was found for $[\mathrm{Co(salen)Na(THF)}]_n$.[7] For understanding the action of the crown ether in causing the loss of carbon dioxide by complexes II, we must refer to the solid-state structure of V.

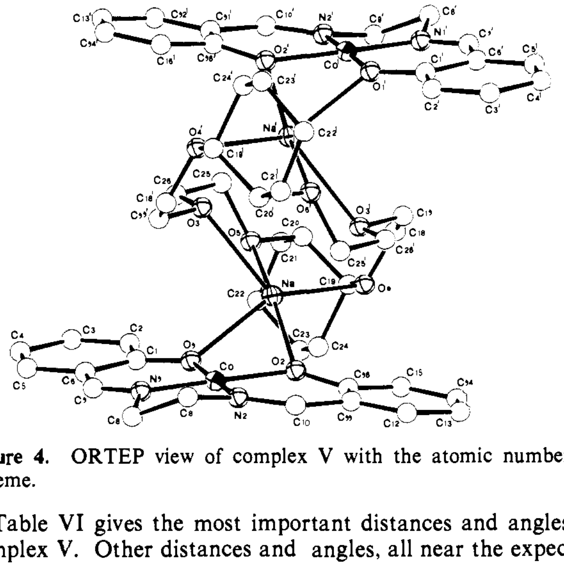

Figure 4. ORTEP view of complex V with the atomic numbering scheme.

Table VI gives the most important distances and angles in complex V. Other distances and angles, all near the expected

Table IV. Selected Bond Lengths (Å) and Angles (Deg) in [Co(*n*-Pr-salen)K(CO_2)(THF)] (Form A)[a]

Co-O(1)	1.88 (1)	K(1)-O(3)	2.69 (2)
Co-O(2)	1.84 (1)	K(1)-O(4)	2.73 (2)
Co-N(1)	1.84 (2)	K(1)-O(5)	2.60 (4)
Co-N(2)	1.91 (2)		
Co-C(1)	1.99 (3)	K(2)-O(1)	2.71 (2)
		K(2)-O(2)	2.69 (1)
C(1)-O(3)	1.24 (3)	K(2)-O(3)	2.60 (2)
C(1)-O(4)	1.22 (4)		
O(1)-Co-O(2)	84.8 (6)	O(1)-K(2)-O(1)'	99.4 (5)
O(1)-Co-N(1)	90.4 (7)	O(1)-K(2)-O(2)	55.3 (4)
O(1)-Co-N(2)	169.2 (7)	O(1)-K(2)-O(2)'	120.3 (4)
O(1)-Co-C(1)	98.5 (9)	O(1)-K(2)-O(3)	67.5 (5)
O(2)-Co-N(1)	169.9 (7)	O(1)-K(2)-O(3)'	157.0 (5)
O(2)-Co-N(2)	92.0 (7)	O(2)-K(2)-O(2)'	174.3 (5)
O(2)-Co-C(1)	98.0 (10)	O(2)-K(2)-O(3)	69.0 (5)
N(1)-Co-N(2)	91.0 (8)	O(2)-K(2)-O(3)'	113.6 (5)
N(1)-Co-C(1)	91.5 (11)	O(3)-K(2)-O(3)'	130.8 (5)
N(2)-Co-C(1)	92.1 (10)		
		O(3)-C(1)-O(4)	134.9 (26)
O(3)-K(1)-O(4)	49.5 (5)	O(3)-C(1)-Co	110.5 (20)
O(3)-K(1)-O(5)	91.7 (8)	O(4)-C(1)-Co	114.2 (20)
O(4)-K(1)-O(5)	83.9 (8)		

[a] Estimated standard deviations in parentheses refer to the last digit.

Table V. Selected Bond Lengths (Å) and Angles (Deg) in [Co(*n*-Pr-salen)K(CO_2)(THF)] (Form B)[a]

Co-O(1)	1.89 (1)	K(1)-O(3)	2.74 (1)
Co-O(2)	1.87 (1)	K(1)-O(4)	2.66 (1)
Co-N(1)	1.91 (1)	K(1)-O(5)	2.70 (2)
Co-N(2)	1.87 (1)		
Co-C(1)	2.00 (2)	K(2)-O(1)	2.75 (1)
		K(2)-O(2)	2.63 (1)
C(1)-O(3)	1.20 (2)	K(2)-O(3)	2.68 (1)
C(1)-O(4)	1.24 (2)		
O(1)-Co-O(2)	84.2 (4)	O(1)-K(2)-O(1)'	93.4 (3)
O(1)-Co-N(1)	90.4 (5)	O(1)-K(2)-O(2)	55.9 (3)
O(1)-Co-N(2)	173.7 (5)	O(1)-K(2)-O(2)'	121.6 (3)
O(1)-Co-C(1)	94.9 (6)	O(1)-K(2)-O(3)	67.4 (3)
O(2)-Co-N(1)	164.3 (5)	O(1)-K(2)-O(3)'	146.9 (3)
O(2)-Co-N(2)	92.7 (5)	O(2)-K(2)-O(2)'	177.1 (4)
O(2)-Co-C(1)	102.6 (5)	O(2)-K(2)-O(3)	70.8 (3)
N(1)-Co-N(2)	91.1 (6)	O(2)-K(2)-O(3)'	110.3 (3)
N(1)-Co-C(1)	92.5 (6)	O(3)-K(2)-O(3)'	141.4 (4)
N(2)-Co-C(1)	91.2 (6)		
		O(3)-C(1)-O(4)	132.0 (15)
O(3)-K(1)-O(4)	48.8 (3)	O(3)-C(1)-Co	113.0 (11)
O(3)-K(1)-O(5)	89.8 (4)	O(4)-C(1)-Co	115.0 (11)
O(4)-K(1)-O(5)	81.1 (4)		

[a] Estimated standard deviations in parentheses refer to the last digit.

Table VI. Interatomic Distances and Angles in Co and Na Polyhedra for Complex V[a]

distances, Å		angles, deg	
Co-O(1)	1.88 (2)	O(1)-Co-O(2)	85 (1)
Co-O(2)	1.91 (2)	O(1)-Co-N(1)	94 (1)
Co-N(1)	1.76 (3)	O(1)-Co-N(2)	178 (1)
Co-N(2)	1.79 (3)	O(2)-Co-N(1)	178 (1)
		O(2)-Co-N(2)	96 (1)
Na-O(1)	2.34 (2)	N(1)-Co-N(2)	86 (1)
Na-O(2)	2.26 (2)		
Na-O(3)	2.58 (1)	O(1)-Na-O(2)	68 (1)
Na-O(4)	2.49 (2)	O(1)-Na-O(3)	90 (1)
Na-O(5)	2.43 (2)	O(1)-Na-O(4)	107 (1)
		O(1)-Na-O(5)	142 (1)
		O(2)-Na-O(3)	129 (1)
		O(2)-Na-O(4)	161 (1)
		O(2)-Na-O(5)	103 (1)
		O(4)-Na-O(3)	68 (1)
		O(5)-Na-O(3)	120 (1)
		O(5)-Na-O(4)	69 (1)

[a] Standard deviations in parentheses refer to the last digit.

Table VII. IR Bands of Carbon Dioxide in Co(R-salen)M(CO_2)L_n Complexes

complex[a]	CO_2 bands,[b] cm^{-1}
Co(salen)Na(CO_2)	1680, 1278, 1212
(Py)Co(salen)Na(CO_2)	1700, 1275, 1208
(Py)Co(salen)K(CO_2)	1680, 1280, 1215
Co(salen)Li(CO_2)	*c*, 1300, 1210
Co(salen)Cs(CO_2)	1650, 1220, *d*
Co(Et-salen)Li(CO_2)(THF)$_{0.5}$	1640, 1295, 1235
Co(Et-salen)Na(CO_2)(THF)	1680, 1287, 1225
Co(*n*-Pr-salen)K(CO_2)(THF)	1650, 1280, 1215
Co(*n*-Pr-salen)K($^{13}CO_2$)(THF)	1610, 1250, 1192

[a] Nujol mulls prepared in a carbon dioxide atmosphere. [b] Strong and sharp bands disappearing on exposure to the air in a few minutes. [c] This band was not identified because it was lower than 1600 cm^{-1}, where the Co(salen) unit shows a complex envelope of bands. [d] Nonidentified band.

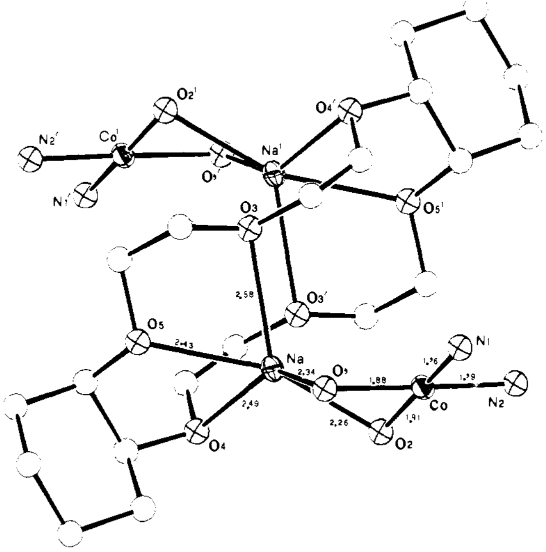

Figure 5. Partial view of the molecule showing the coordination polyhedra around Co and Na in complex V.

values, have been deposited as supplementary material. An ORTEP[24] view of the molecule of the complex is shown in Figure 4. The atoms of the complex are arranged around the inversion centers at $^1/_2$, $^1/_2$, $^1/_2$ and 0, 0, $^1/_2$, so the asymmetric part of the structure is a half-molecule, namely one Co(salen) group, and one Na atom, and one-half of dicyclohexano-18-crown-6 ether. Between the molecules of the complex are located THF solvent molecules. Their high thermal parameters may be ascribed to positional disorder or statistical occupancy or both. The crystal structure is therefore built up by the neutral ([Co(salen)Na]$_2$–dicyclohexano-18-crown-6 ether) units and THF molecules held together by van der Waals interactions. The intermolecular distances are regular. Each Na atom is 5-fold coordinated according to an irregular polyhedron: sodium links the two oxygen atoms of one Co(salen) group and three oxygen atoms of the macrocyclic ligand. Na–O distances range between 2.26 (2) and 2.58 (1) Å (average value 2.42 Å). A distance 2.78 (1) Å occurs between Na and O(3′), which is linked also to Na′ (the apex indicates atoms related by the inversion center). A partial view of the molecule showing the two coordination squares around cobalt atoms and two polyhedra around sodium atoms is presented in Figure 5. The salen coordination around cobalt is nearly planar, the deviation of the cobalt atom from the least-squares plane through the four donor atoms being 0.004 Å. The Co–O and Co–N distances are in close agreement with those found in similar bifunctional complexes.[7] The Co–N bond lengths (Co–N mean

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(24) Johnson, C. K. ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1975.

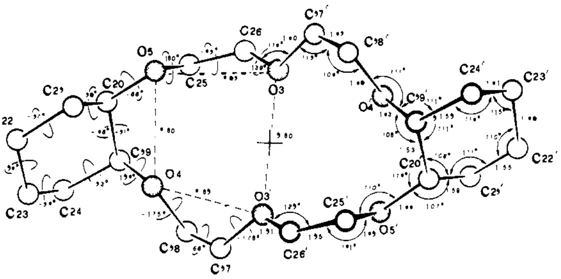

Figure 6. View of the dicyclohexano-18-crown-6 ether with interatomic distances, angles, and torsion angles. Estimated standard deviations are 0.04 Å for distances of 2°–3° for angles.

value 1.78 Å), are shorter than the 1.91-Å value observed for several Co(salen) derivatives[21,25] and in this case may be probably ascribed to the low oxidation state of cobalt. The other distances and angles of salen fall in the usual range. The ethylene bridge has a nearly "gauche" conformation [N(1)–C(8)–C(9)–N(2) torsion angle: −34°]. The diocyclohexano-18-crown-6 ether is present as the cis–anti–cis isomer, as in the NaBr complex.[26] The macrocycle conformation is significantly distorted from the symmetric "crown" models observed in some previous studies, because of the geometrical constraints imposed by the guest ions strongly bonded to groups of great hindrance as the Co(salen). The six oxygen atoms of the macrocyclic ring lie alternatively below and above their mean planes (the deviation from the best plane is up to 0.24 Å) and form an irregular hexagon contracted along the diagonal O(3)–O(3′). In this way, each of the two Na ions located above and below the oxygen plane with positions shifted from the center of the ring has three oxygen atoms as nearest neighbors (average distance 2.50 Å) and one at longer distance (2.7 Å). The polyether is shown in Figure 6, where the crystallographic numbering of the atoms as well as selected distances and angles are reported, together with the values of torsion angles.

The cyclohexane ring has the chair conformation. Torsion angles are all satisfactorily within the ideal range of 60°, the average value being 55°. C–C bond distances average 1.53 Å, in agreement with the expected value for C in sp^3 hybridization. The dihedral angle between the best plane through the cyclohexyl and the plane of oxygen atoms of the crown ether is 123°. The structure of V shows that the bifunctional cobalt(I)–sodium unit remains intact, but all the coordination sites around the alkali cation are filled by the polyether, so that any acid site is not further available for binding CO_2. The presence of a free nucleophilic cobalt(I) in complex V, where it maintains the same characteristics as in Co(salen)Na(THF), is not enough for binding CO_2.

We can remember that the "leit-motiv", which pervades CO_2 chemistry, is the request of a bifunctional system for its activation even in the most simple reactions. As suggested by R. J. P. Williams,[6] the hydration of CO_2 catalyzed by biphilic oxoanions, the carboxylation of sodium phenoxide and carbonic anhydrase assisted hydration of CO_2 can be viewed as the consequence of a fundamental step in which CO_2 interacts with an acid–base system.

On the basis of the results and considerations outlined above, the main function of the (R–salen) ligand can be viewed as being able, because of the presence of bicovalent oxygens, to coordinate both a cobalt(I) and an alkali cation. It must be added that the electronic flexibility of the polydentate ligand and its symbiosis with the transition metal give rise to the stabilization of a wide range of interrelated oxidation states for cobalt. This property makes possible Co(salen)–O_2 chemistry involving an easy Co(II)–Co(III) interconversion[28] as well as Co(salen)Na–CO_2 chemistry requiring, as reported in reaction 1, a cobalt(I)–cobalt(III) reversible change.

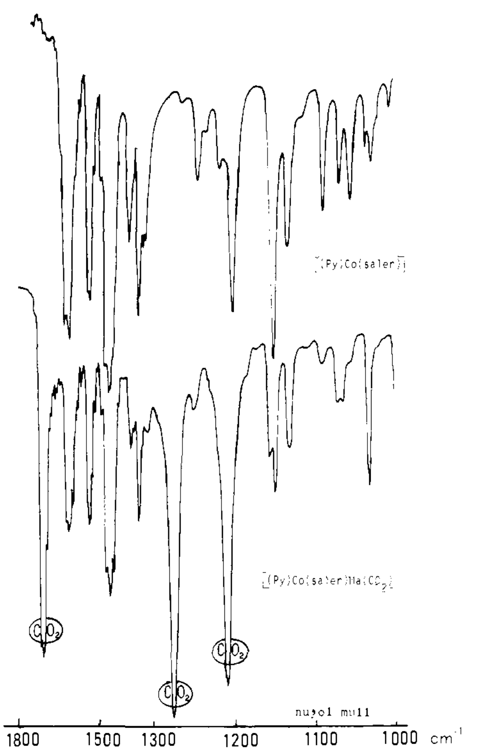

Figure 7. IR spectra (Nujol mull) of (Py)Co(salen) and (Py)Co(salen)Na(CO_2).

We have also observed, as has also been reported for Co(salen)–O_2[9,28] chemistry, that the presence of different substituents on the salen has a rather limited effect on the relative stability of the CO_2 complexes and on the characteristics of the bonded CO_2.

An important, although indirect, role played by the salen-like ligand is in determining the relative solubility of the CO_2 complexes, making possible the isolation in the solid state of complexes II. Concerning this point, we must examine the influence of two other interrelated factors on reaction 1 and on the nature of the complexes II, namely the nature of the alkali cation and of the reaction solvent. With a look to the "action" of complexes I as depicted in reaction 4, it is evident that the nature and the availability of coordination sites on the alkali cation is a critical point. The left-shifted equilibrium in the absorption of CO_2 by Co(salen)Li$(THF)_{1.5}$ in THF or Py solutions means that the Lewis acid center prefers the solvent over the oxygens of CO_2.

On the other hand, when a lithium complex such as Co(Et-salen)Li(CO_2) is isolated from a THF solution, it is, at least from a qualitative point of view, the most stable CO_2 complex, since it did not lose CO_2 in the air or in vacuo when in the solid state. This is a consequence of a strong O–M interaction, which could be higher for Li^+ than for other alkali cations. The IR spectrum showed, in fact, for both lithium derivatives, the lowest C–O stretching frequencies (Table VII). Another factor that could introduce a Co–CO_2 stabilization, that is, a Co–C bond stabilization, could be the utilization of potentially coordinating solvents for cobalt(III). Once again we can consider a parallel between Co(salen)–O_2 and Co(salen)M–CO_2 chemistries. The utilization of pyridine vs. other less coordinating solvents like DMF, Me_2SO, etc. seems to introduce a stabilization factor on a Co–CO_2 bond, as was observed for $[(Py)Co(salen)]_2O_2$, which is significantly less reversible than the corresponding $[Co(salen)]_2O_2$ or $[(DMF)Co(salen)]_2O_2$.[9] The function of the axial ligand Py can be viewed in both cases as influencing the possible redox potential for Co(II)–Co(III) and Co(I)–Co(III) couples.[28]

The first diagnostic tool for looking at the "status" of the bonded CO_2 is to use IR spectra. Figures 7–9 report the following compared spectra: Co(salen)(Py) and (Py)Co(salen)Na(CO_2), Figure

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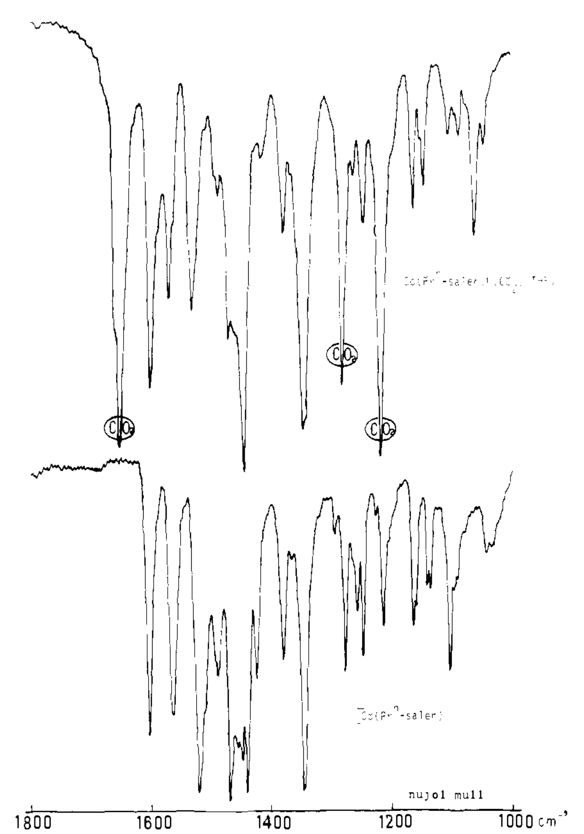
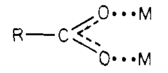


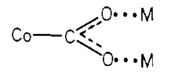
Figure 8. IR spectra (Nujol mull) of Co(n-Pr–salen) and Co(n-Pr–salen)K(CO_2)(THF).

7; Co(n-Pr–salen) and Co(n-Pr–salen)K(CO_2)(THF), Figure 8; Co(n-Pr–salen)K(CO_2)(THF) and Co(n-Pr–salen)K($^{13}CO_2$)(THF), Figure 9.

The status of coordinated CO_2, as deduced from the IR spectrum, is very similar in all complexes independent of the nature of the ligand R–salen and only slightly dependent on the nature of the alkali cation (Table VII). The very low solubility of all CO_2 complexes II prevents any determination of IR spectra in solution. Therefore any comparison between solid state and solution of CO_2 bonding modes to a complex cannot be done. The spectra usually show three sharp and strong bands for a reduced form of CO_2 in a bent arrangement. This spectrum looks like that of a carboxylato group (A) binding two metal centers (M):[29]



A



B

the C–O band frequencies are significantly different for A vs. B because of the strong difference between the organic group R and cobalt in terms of electron-donating ability.[29]

The activated "status" of coordinated CO_2 indicated from the structural and spectroscopic data raises the question why the fixation of CO_2 is not followed in this case, as usually, by one of its elementary transformations. All the "nucleophilic" metals used in CO_2 fixation led, except in a few cases[4,30] in which CO_2 is fixed in its intact form, to the head-to-tail dimerization preceding the "so-called" disproportionation to CO_3^{2-} and CO.[3,5,31] This was observed even when the similar "bifunctional" metal carbonyl anions have been used.[32] Therefore it seems that the stereochemical rigidity of the "bifunctional" unit may have an essential role.

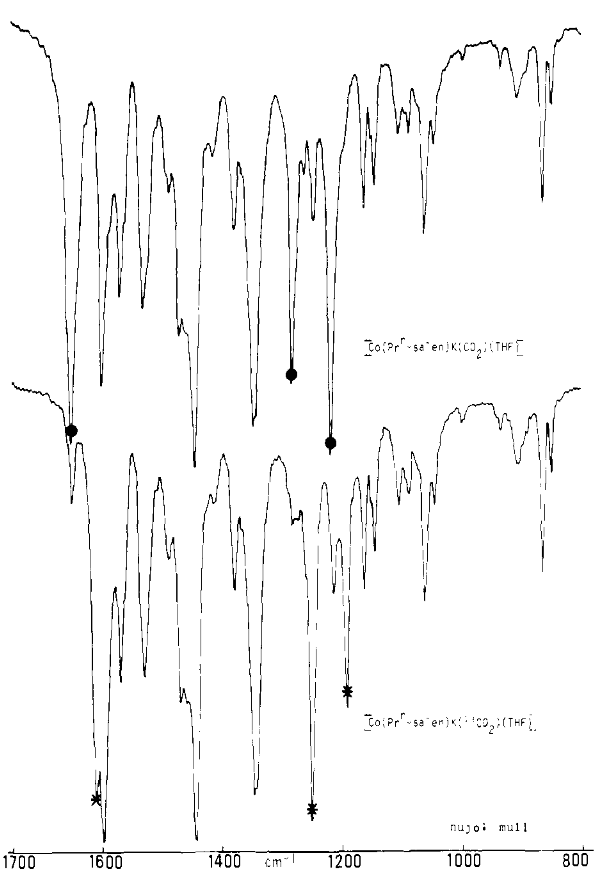


Figure 9. IR spectra (Nujol mull) of Co(n-Pr–salen)K(CO_2)(THF) and Co(n-Pr–salen)K($^{13}CO_2$)(THF).

Since the two-electron reduction of CO_2 by cobalt(I) becoming cobalt(III) in complexes II generates potentially nucleophilic oxygens susceptible to electrophilic attack, we tried to perform the alkylation of coordinated CO_2 in complexes II, using various alkylating agents such as $PhCH_2Cl$, MeI, $(Me)_2SO_4$, Et_3O^+, etc.[30] All these reactions led, however, to the alkylation of cobalt rather than of CO_2, forming the corresponding alkyl R–Co(salen)[33] complexes rather than the esters [(salen)CoC(O)OR)]. This is, we believe, since in all solvents we have in equilibrium the free nucleophilic cobalt(I) along with the reduced CO_2 bonded to cobalt(III) (reaction 1), even if for a very small extent, and the employed electrophiles strongly prefer the soft cobalt(I) vs. the hard oxygen.

In conclusion, we can say that the perspectives in CO_2 activation by means of the proposed models results in (i) the possibility of performing reactions on coordinated CO_2 (this requires the absence of the equilibrium reported in reactions 1 and 4) and (ii) achievement of the possibility for controlling the extent of electron transfer from cobalt to CO_2, which involves two electrons for the reported fixation. As we noticed with CO_2-like molecules, metal–CO_2 interactions involving one-electron transfer can lead to a C–C bond formation, which represents one of the most promising metal-assisted transformations of CO_2.[34]

Acknowledgment. We thank CNR (Rome) for financial support.

Registry No. [Co(Et-salen)], 82536-87-6; [Co(Pr-salen)], 82536-88-7; [Co(CH_3COO)$_2$], 71-48-7; [Co(salen)]Cs, 82536-89-8; [Co(salen)], 14167-18-1; [Co(Pr-salen)]K, 68866-09-1; [Co(Et-salen)]Li, 82536-90-1; [Co(salen)]Li, 59699-75-1; CO_2, 124-38-9; [(Py)Co(salen)Na(CO_2)], 82536-91-2; [Co(salen)Li(CO_2)], 82597-19-1; [Co(salen)]Na, 15053-

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51-7; [Co(salen)Na(CO_2)], 82570-84-1; [Co(salen)]K, 82536-92-3; [(Py)Co(salen)K(CO_2)], 82536-93-4; [Co(salen)Cs(CO_2)], 82570-85-2; [Co(Et-salen)Li(CO_2)], 82536-94-5; [Co(Et-salen)Na(CO_2)], 82536-95-6; [Co(Pr-salen)K(CO_2)(THF)], 82536-97-8; [Co(salen)Na]$_2$(DCHC), 82536-99-0.

Supplementary Material Available: A listing for structure factor amplitudes for complexes [Co(*n*-Pr–salen)K(CO_2)(THF)] (form A), [Co(*n*-Pr–salen)K(CO_2)(THF)] (form B), and complex V; Interatomic distances for (*n*-Pr–salen) ligand are listed in Table VIII (form A) and Table IX (form B); calculated fractional atomic coordinates for hydrogen atoms of form B (Table X) and of complex V (Table XI); bond distances and angles for the Co(salen) group in complex V (Table XII) (14 pages). Ordering information is given on any current masthead page.

Synthetic, Structural, and Physical Studies of Bis(triethylammonium) Tris(catecholato)vanadate(IV), Potassium Bis(catecholato)oxovanadate(IV), and Potassium Tris(catecholato)vanadate(III)

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Abstract: The syntheses, properties, and crystal structures of the complexes $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$, $K_3[V(cat)_3]\cdot 1.5H_2O$, and $K_2[VO(cat)_2]\cdot EtOH\cdot H_2O$ are described. The complex $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$ [$P2_12_12_1$, with a = 10.473 (1) Å, b = 10.794 (1) Å, and c = 29.986 (3) Å; Z = 4; ρ_{calcd} = 1.216; ρ_{obsd} = 1.21 g cm^{-3}; R_w = 7.2%] consists of a novel vanadium(IV) octahedral complex [V–O bond length 1.930 (3) Å; O–V–O bond angle 88.8°] in which catechol has displaced the vanadyl oxygen. In contrast, $K_2[VO(cat)_2]\cdot EtOH\cdot H_2O$ [$P2_1/c$ with a = 14.380 (1) Å, b = 12.307 (2) Å, and c = 11.187 (1) Å, β = 111.80°; Z = 4; ρ_{calcd} = 1.537; R_w = 7.8%] is a typical square-pyramidal vanadyl complex: V=O bond length of 1.616 (4) Å, the vanadium 0.58 Å out of the basal plane, and average V–O(catechol) bond lengths of 1.956 Å. The complex $K_3[V(cat)_3]\cdot 1.5H_2O$ [$C2/c$, with a = 20.727 (4) Å, b = 15.884 (2) Å, c = 12.312 (2) Å, and β = 91.46°; Z = 8; ρ_{calcd} = 1.703; R_w = 4.6%] closely approximates octahedral symmetry about the metal and is isostructural with the Cr and Fe analogues. In addition to the synthesis and structures of these complexes, we report the results of optical, infrared, and electron paramagnetic resonance spectroscopy, as well as electrochemical and magnetic studies for the complexes VOL, VOL_2, and VL_3 (where L = catechol, 4,5-dihydroxybenzene-1,3-disulfonate and 3,5-di-*tert*-butylcatechol). The unprecedented feature of these results is observation of a tris octahedral structure for a vanadium(IV) complex in water. This remarkable displacement of the vanadyl oxygen is attributable to the exceptional chelating ability of catechol and its great affinity for highly charged metal ions—similar to that of hydroxide. The extensive, and often contradictory, literature of this field is reconciled and the claims for reversible O_2 binding by a V(IV) catecholate species are shown to be spurious.

As part of our studies of transition-metal complexes with siderophores,[4] in particular those of the catechol (*o*-dihydroxybenzene) type, we have been led to include studies of the parent ligand, catechol itself. In the present report the interaction of catechol with vanadium is described, an interaction which, despite having seen numerous studies, is still characterized by confusion in the literature. The failure to isolate and characterize complexes structurally has largely been responsible for the puzzlement about whether vanadium(IV) forms a tris complex with catechol or a vanadyl bis(catecholate) and the question of whether the V(V) complex is capable of existence. Despite this confusion, the deep blue color produced by interaction of V(IV) or V(V) with catechol has been of analytical value,[5] even though the nature of the blue species was unclear.

Early studies by Rosenheim and Mong[6] led these workers to suggest for their deep blue product a vanadyl bis(catecholate) structure with a catechol of crystallization, apparently in the belief that the very stable vanadyl group could not be displaced.

This belief subsequently appeared to be supported by numerous[7-11] potentiometric studies, in which an end point was found at 4 mol of alkali/mol of vanadium (independent of the catechol/vanadium ratio); this was taken to indicate that the terminal member of the coordination series was the vanadyl bis(catecholate).

However, in contradiction to this conclusion, Henry, Mitchell, and Prue[12] in the definitive work to date found that thallous salts precipitated a complex, which analysis indicated is the tris complex $Tl_2[V(cat)_3]$ (with 1.7 μ_B magnetic moment) but which unfortunately is completely insoluble in solvents with which it does not react.

Despite the isolation of complexes with 3:1 ligand:metal stoichiometry by Rosenheim et al. and by Henry et al., another potentiometric study by the latter authors[13] also failed to provide

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