Structure and Reactivity of Sodium Phenoxide – Following the Course of the Kolbe-Schmitt Reaction

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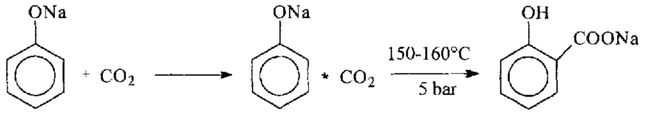
Solvent-free sodium phenoxide (NaOPh) crystallises as a polymer and forms a polymeric chain in the [0 0 1] direction. The low coordination of the sodium atoms, as evident in the crystal structure, is confirmed by the easy coordination of oxoligands (σ-donors). Hence, the four-membered ring chain of the solvent-free sodium phenoxide is separated by oxoligands, and forms partial structures as the polymer fragments. Thus, NaOPh crystallises in THF with the formation of an Na_6O_6 core, consisting of two face-fused heterocubes, and in *N,N,N',N'*-tetramethyl urea (TMU) with the formation of a Na_4O_4 heterocubane. The solvent-free NaOPh–CO_2 complex obtained from the addition of CO_2 to a solution of sodium phenoxide is, when exposed to a temperature of 80 °C, subject to an irreversible phase transition, as demonstrated by FT-IR and DTA studies. The complex formed at 80 °C is, apparently, another intermediate of the Kolbe-Schmitt reaction.

In 1885, Schmitt succeeded in carrying out the carboxylation of sodium phenoxide to salicylic acid, which had previously been shown by Kolbe in 1860, in high yield (Scheme 1)[1][2]. The Kolbe-Schmitt reaction has been used on an industrial scale since 1874[3].

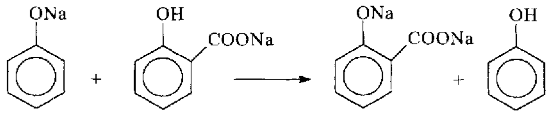
A sodium phenoxide–CO_2 complex is discussed as a potential intermediate. It is formed after many hours of contact of sodium phenoxide with CO_2 at room temp., and was studied by means of FT-IR[4]. The complex is assumed, on heating to 150 °C under a pressure of 5 bar, to react to give the monosodium salt of salicylic acid. Schmitt suggests that, in an additional side reaction, uncomplexed sodium phenoxide reacts with the already formed monosodium salicylate to give disodium salicylate and phenol (Scheme 2)[2], which leads to a reduction in the yield of salicylate. It follows that the precondition for a high yield of monosodium salicylate is a quantitative formation of the intermediate complex of NaOPh with CO_2.

The X-ray crystal structure of 4-methyl-substituted sodium phenoxide has been described previously[5]. However, the crystal structure of unsubstituted NaOPh, and reliable findings on the thermal stability of the intermediates, have not yet been reported. In this paper, we present the crystal structures of both sodium phenoxide and several of its complexes with oxoligands. Additionally, we report on the complexation of NaOPh by CO_2, and the thermal behaviour of the complex as shown by means of FT-IR and DTA. The aim was to provide a better insight into the course of the Kolbe-Schmitt reaction.

Scheme 1. Reaction of NaOPh with CO_2 to sodium salicylate



Scheme 2. Side reaction of the Kolbe-Schmitt reaction



Results and Discussion

The crystal structure of sodium phenoxide, an essential prerequisite for the interpretation of the Kolbe-Schmitt reaction[4][6], is now available. Crystals of solvent-free NaOPh were cultivated using Bridgmann-Stockbagger apparatus[7]. The crystal structure exhibits polymeric chains resulting from the stacking of the Na_2O_2 four membered ring chains which propagate along the [0 0 1] direction (Figure 1 and 2)[8]. The four-membered rings are the central unit of the sodium phenoxide structure. The two Na–O distances in the four-membered rings are 2.334(6) Å and 2.328(6) Å.

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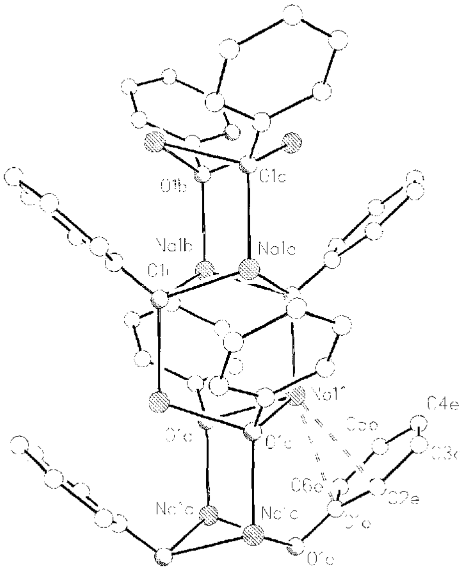
The sodium atoms Na1b and Na1d couple the upper four-membered ring with two bonds in the positive *z*-direction, while the atoms O1i and O1f couple the lower four-membered ring in the opposite direction [distance 2.264(1) Å]. This alternating coupled binding results in a compression of the four-membered rings to a dome-like structure. On the other hand, the distances Na1f–O1e are elongated to 3.614(7) Å due to the compression of the four-membered rings. The coordination number of four of the sodium atoms is achieved by the interaction with a η^6-arene ring from the next Na_2O_2 unit. The shortest Na–C distances are 2.81(1) Å (Na1f–C1e, *ipso*) and 2.79(1) Å (Na1f–C2e, *ortho*). The Na–C(η^6-arene) average distance of 3.05(8) Å is similar to the average Na–C(η^6-arene) distances of 2.94(11) Å in sodium 4-methylphenoxide[5][9]. This can be regarded as an interaction with the olefinic π-system as defined by Schade and Schleyer (2.72 Å)[10]. The interaction with the bulky phenyl groups leads to a remarkable low-coordinated sodium ion.

Figure 1. Crystal structure of NaOPh[a]



[a] Selected distances [Å] and angles [°]: Na1f–O1f 2.2636(8), Na1f–O1c 2.328(6), Na1f–O1a 2.334(6), Na1f–O1e 3.614(6), Na1f–C1e 2.81(1), Na1f–C2e 2.79(1), Na1f–C3e 3.02(1), Na1f–C4e 3.37(1), Na1f–C5e 3.30(1), Na1f–C6e 3.13(1), Na1f–Na1i 3.24(1), Na1f–Na1b 3.651(5), O1e–C1e 1.33(1), C1c–C2e 1.41(1), C1e–C6e 1.42(1), Na1f–O1c–Na1i 105.3(3), O1f–Na1f–O1c 103.8(3), O1f–Na1f–O1a 103.4(3), O1c–Na1f–O1a 84.6(4), O1f–Na1f–C1e 160.5(4), O1c–Na1f–C1e 90.3(2), O1a–Na1f–C1e 91.2(3).

The Na_2O_2 polymeric chains undergo fragmentation if subjected to oxoligands in the form of aprotic polar solvents. This results in hexameric and tetrameric aggregates under coordinative saturation of the sodium ions, and thus it was possible to generate a hexameric aggregation, with the formation of an Na_6O_6 hetero-face-fused double cubane, on crystallisation of NaOPh from THF (Figure 3)[8]. The coordinative saturation of the sodium cations results from three or four oxygen atoms of the phenoxide ions and one oxygen atom of the solvent.

Figure 2. The three-dimensional structure of NaOPh looking down the crystallographic *c* axis

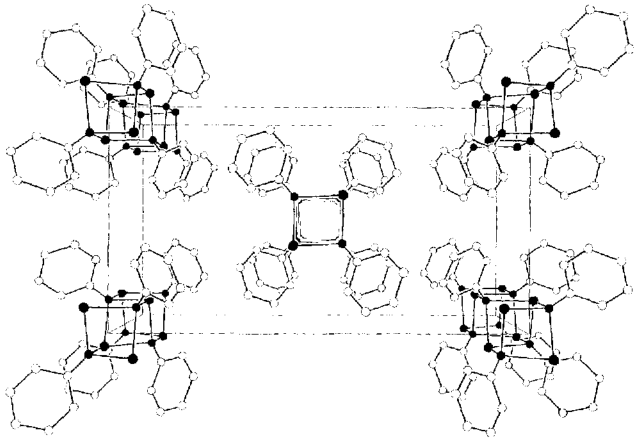
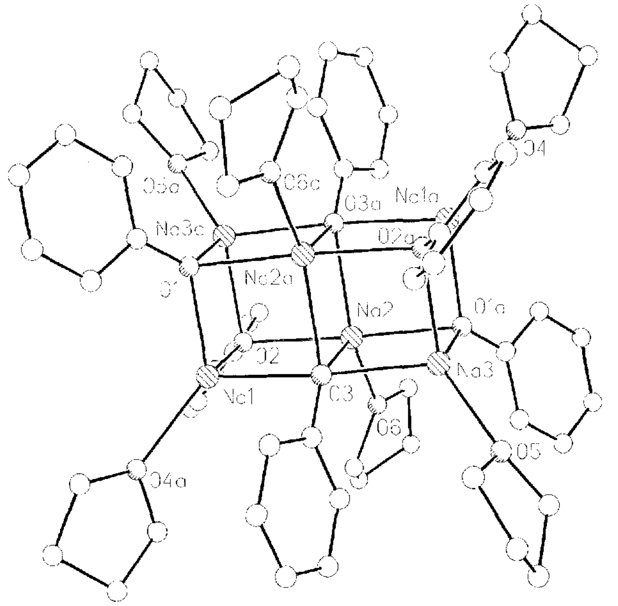


Figure 3. Crystal structure of NaOPh·THF[a]

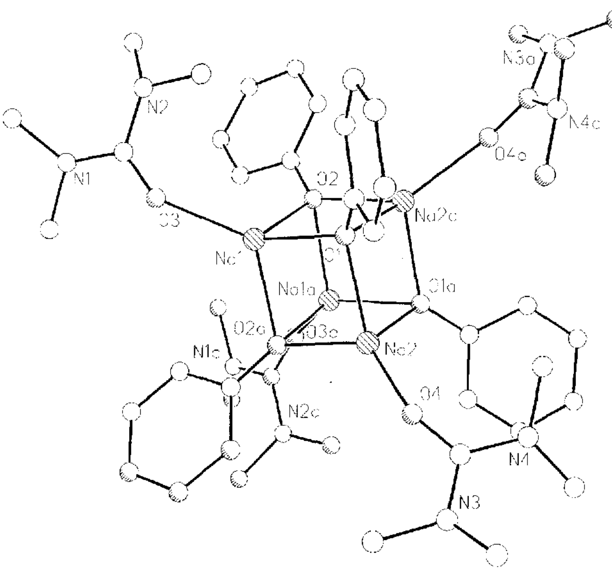


[a] Selected distances [Å] and angles [°]: Na1–Na2 3.310(2), Na2–Na3 3.263, Na1–O3 2.403(2), Na1–O2 2.231(3), Na1–O1 2.256(2), Na1–O4a 2.278(2), Na2–O2 2.365(2), Na2–O3a 2.405(2), Na2–O3 2.376(2), Na2–O1a 2.363(2), Na2–O6 2.318(3), O3a–Na2–O3 89.45(8), O3–Na2–O6 124.86(9), O6–Na2–O3a 145.68(9), O2–Na2–O1a 176.40(9), O1–Na1–O3 91.23(8), O2–Na1–O1 93.44(9), O4a–Na1–O3 123.69(9), Na1–Na2–Na3 92.78(5).

Using *N,N,N′,N′*-tetramethyl urea (TMU), a highly polar ligand with a high steric demand as a solvent, it was possible to obtain a system with even lower aggregation. NaOPh·TMU (1:1) crystallises to give a Na_4O_4 heterocubane (Figure 4)[8]. The sodium cations are coordinated in a distorted tetrahedral fashion by three phenoxide oxygen atoms and one oxygen atom from one TMU molecule.

X-ray structures of this type have been described before[11]. Whereas the Na_4O_4 heterocube constitutes a frequently observed structural motif in phenoxide solvent complexes[12], there is only one example of a hexameric

Figure 4. Crystal structure of NaOPh·TMU[a]



[a] Selected distances [Å] and angles [°]: Na1−Na2 3.216(2), Na1−Na2a 3.251(5), Na1−O1 2.290(4), Na1−O2 2.282(3), Na1−O2a 2.310(4), Na1−O3 2.217(3), Na2−O1 2.277(4), Na2−O1a 2.315(4), Na2−O4 2.197(4), O3−Na1−O1 137.8(2), O1−Na1−O2 89.6(1), O3−Na1−O2a 123.2(1), O1−Na1−Na2 45.1(1), C1−Na1−O1 126.5(1).

double cube Na_6O_6[13], and two examples of the dimeric units Na_2O_2[14]. In all structurally characterised NaOPh solvent complexes, the coordination of the oxygen of the ligand leads to the break-up of the four-membered ring chain of NaOPh. Depending on the polarity and the steric demand of the ligand, different partial structures of the polymer are formed.

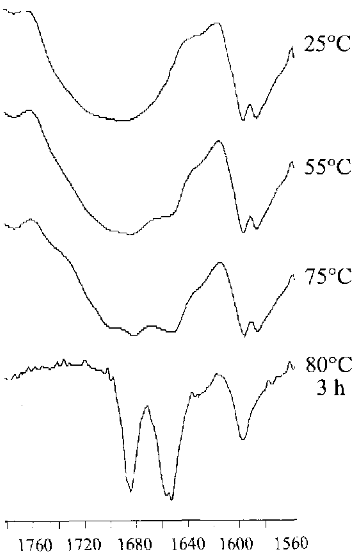
In our opinion, the coordination of the oxoligand CO_2 during the course of the Kolbe-Schmitt reaction leads to the interaction with the potentially free coordination sites at the sodium atoms. The four-membered ring chain of NaOPh is destroyed. The reaction at 25 °C leads to a molar ratio of NaOPh/CO_2 = 1:1[2][6].

We obtained such a solvent-free NaOPh−CO_2 complex by exposing a sodium phenoxide solution to CO_2. The yield is particularly high in THF or dioxane, and in TMU at low temperature. The originally coordinated solvent is displaced and replaced by CO_2 and the unsolvated complex NaOPh−CO_2 precipitates as a white amorpheous solid. The molar ratio of 1:1 was established using gas volumetric analysis. Contrary to the solid state reaction, which lasts several hours, the uptake of an equimolar amount of CO_2 and the subsequent precipitation of the complex at room temp. is completed after a few minutes.

There has been controversial discussion concerning the thermal stability of the complex NaOPh−CO_2 in previous investigations into the mechanism of the Kolbe-Schmitt reaction. Tijmstra assumes that decarboxylation occurs as soon as the temperature exceeds 80 °C[15] and that, on increasing the temperature, a direct carboxylation of the phenyl ring takes place; the high selectivity of carboxylation in the *ortho* position is not explained. On the other hand, Davies discusses the formation of an intermediate at 80 °C based on vapour pressure diagrams and supports the idea of a subsequent rearrangement reaction of the complex to sodium salicylate[16].

We carried out FT-IR studies on the thermal behaviour of the NaOPh−CO_2 complex obtained from THF. The complex was suspended in CO_2-saturated nujol and heated stepwise to 80 °C by means of a thermocontrolled KBr cuvette (Figure 5). At 55 °C, formation of a shoulder at the asymmetric stretching vibration, $\tilde{\nu}(CO_2)$asym = 1685 cm^{-1}, was visible. A slight shift of $\tilde{\nu}(CO_2)$asym, and the simultaneous splitting of the vibration into the bands at 1680 cm^{-1} and 1651 cm^{-1}, occured after further heating to 75°C. The splitting is thermally irreversible. Figure 5 also shows the FT-IR spectrum of a powdery NaOPh−CO_2 complex after a 3 h thermal treatment at 80 °C under a CO_2 atmosphere, which was obtained in a further experiment. The clearly visible splitting of the bands reveals a phase transition of the complex and shows that a further intermediate of the Kolbe-Schmitt reaction is formed.

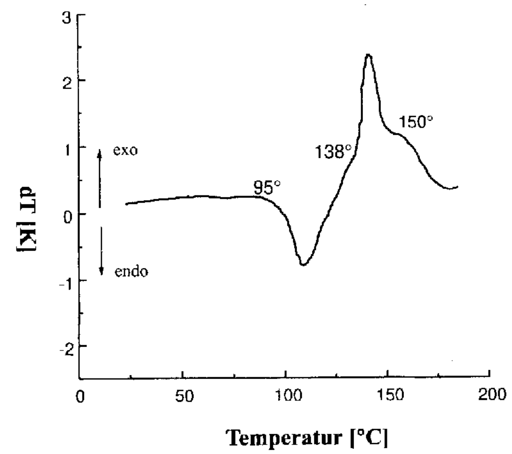
Figure 5. FT-IR study of the NaOPh-CO_2 complex on temperature increase



The results of the IR investigations are supported by the observation of thermal effects by means of DTA measurements. Starting from the solvent-free NaOPh−CO_2 complex, the complete reaction to sodium salicylate and the successive formation of disodium salicylate was followed by means of DTA (Figure 6).

The endothermic process occurring at 95 °C is in good accordance with the splitting of the $\tilde{\nu}(CO_2)$asym vibration band observed in this temperature range in the FT-IR spectrum. As could be shown with HPLC, the carboxylation of sodium phenoxide had not yet taken place. The formation of sodium salicylate is only observed after a further rise in temperature (130−140 °C) and correlates with the exothermic process observed at 138 °C in the DTA spectrum. The reaction enthalpy for the Kolbe-Schmitt reaction has been reported to be −90 kJ/mol[3].

Figure 6. DTA study of the NaOPh$-CO_2$ complex



The shoulder in the DTA spectrum at 150 °C is most likely due to the competitive side reaction of the already formed sodium salicylate with uncomplexed sodium phenoxide according to Scheme 2[2].

In order to obtain a better quantitative understanding of the NaOPh$-CO_2$ system, further DSC and HPLC studies are in progress.

Conclusions

On the basis of the solvent-free NaOPh$-CO_2$ complex, it was possible to follow the carboxylation of NaOPh completely. The decomplexation of NaOPh during a temperature rise followed by direct carboxylation, as discussed by Tijmstra[13], can be excluded as the reaction pathway of the Kolbe-Schmitt reaction. Comparative investigations of the thermal behaviour of KOPh under CO_2 pressure should provide fundamental information on the selectivity of ring carboxylation.

Based on the crystal structure of NaOPh, the polymeric chain fragmentation was demonstrated in the crystal structures of the complexes $(NaOPh)_6(THF)_8$ and $(NaOPh)_4(TMU)_4$. The reaction of NaOPh with CO_2 could be performed in both the solid state and solution. During uptake of CO_2 the originally coordinated solvent is displaced. It is replaced by CO_2 and a solvent-free complex is formed. Thus, although we could show the structural variation of NaOPh on complexation by oxoligands, the structure of the NaOPh$-CO_2$ complex is still under intense scrutiny.

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Experimental Section

The synthesis of sodium phenoxide was carried out under an argon atmosphere as previously described[17]. The procedure was modified by carefully adding pieces of 2.6 g (113 mmol) of sodium to a solution of 10.0 g (106 mmol, sublimated before use) of phenol in 200 ml of dioxane. The solution was refluxed for 4 h. After cooling to room temp., the excess sodium was separated over a D4 sintered glass. The filtrate was concentrated in vacuo and the product precipitated after addition of 100 ml of petroleum ether. The white residue was filtered off, washed with petroleum ether (2 × 50 ml) and dried in vacuo. – Yield: 11.3 g (92%). – M.p. 380 °C. – IR (KBr): $\tilde{\nu}$ = 1578 cm^{-1}, 1480 (C=C), 1166, 768, 700 (C–H). – ^1H NMR ($[D_8]THF$): δ = 6.19 (t,t, 1 H, C*H*, *para*), 6.42 (d,d, 2 H, C*H*, *ortho*), 6.87 (d,d, 2 H, C*H*, *meta*). – ^{13}C NMR ($[D_8]THF$, 25 °C): δ = 170.5 (*C*–O, ipso), 112.4 (*C*H, *para*), 119.5 (*C*H, *ortho*), 129.7 (*C*H, *meta*).

Crystallisation of Sodium Phenoxide for X-Ray Analysis: The powder was filled into a quartz capillary under an argon atmosphere and sealed. The capillary was introduced into the drilled hole of a heatable copper block, heated to 380 °C and then slowly pulled out within 24 h (according to the procedure of Bridgman and Stockbagger)[7]. Colourless crystals; C_6H_5NaO, crystal structure analysis: 0.35 × 0.08 × 0.08 mm, orthorhombic, *Iba*2, a = 10.375(2), b = 19.404(9), c = 5.698(4) Å, $\alpha = \beta = \gamma = 90°$, V = 1147.1(7) $Å^3$, T = −90 (1) °C, D_{calcd} = 1.34 Mgm^{-3}, 2 $\theta_{max.}$ = 40.0°, 534 independent reflections, 249 $[I > 2\sigma(I)]$ reflections observed, 72 parameters, R $[I > 2\sigma(I)]$ = 0.050, wR = 0.082, largest diff. peak and hole: 0.044 and −0.010 $eÅ^{-3}$.

Crystallisation of Sodium Phenoxide–Solvent Complexes: A hot saturated solution of NaOPh in the respective aprotic polar solvent was allowed to cool to room temp. and then filtered to separate it from crystallites. Colourless crystals suitable for X-ray structure determination were grown in the filtrate after a few days.

$(NaOPh)_6(THF)_8$: Colourless crystals (decomposition at room temp. on filtration from excess solvent); $(C_6H_5NaO)_6 \cdot (C_4H_8O)_8$, crystal structure analysis: 0.4 × 0.38 × 0.36 mm, triclinic, $P\bar{1}$, a = 11.820(4), b = 11.978(3), c = 13.612(5) Å, α = 107.49(3)°, β = 99.38(3)°, γ = 102.45(2)°, V = 1740(1) $Å^3$, T = −90 (1)°C, $D_{calcd.}$ = 1.21 g cm^{-3}, 2 $\theta_{max.}$ = 45.0°, 5932 independent reflections, 5800 $[I > 2\sigma(I)]$ reflections observed, 397 parameters, R $[I > 2\sigma(I)]$ = 0.069, wR = 0.183, largest diff. peak and hole: 0.417 and −0.046 $eÅ^{-3}$.

$(NaOPh)_4(N,N,N',N'$-tetramethylurea$)_4$: Colourless crystals (decomposition at room temp. on filtration from excess solvent); $(C_6H_5NaO)_4 \cdot (C_4H_{12}O)_4$, crystal structure analysis: 0.61 × 0.51 × 0.48 mm, monoclinic, *P*2/*c*, a = 22.473(4), b = 12.860(4), c = 19.703(3) Å, α = 90°, β = 112.44(2)°, γ = 90°, V = 5263(2) $Å^3$, T = −90 (1) °C, $D_{calcd.}$ = 1.172 g cm^{-3}, 2$\theta_{max.}$ = 55.2°, 5972 independent reflections, 3621 $[I > 2\sigma(I)]$ reflections observed, 289 parameters, R $[I > 2\sigma(I)]$ = 0.105, wR = 0.297, largest diff. peak and hole: 0.666 and −0.660 $eÅ^{-3}$.

Synthesis of the Sodium Phenoxide–CO_2 Complex: 5.0 g (43 mmol) of NaOPh was dissolved in 100 ml of THF, and CO_2 was introduced on stirring. A white precipitate formed after a few minutes, and the introduction of CO_2 was continued for 1 h. The suspension was filtered and the residue washed with CO_2-saturated diethyl ether. Drying in a current of CO_2 yielded: 4.91 g (89%) $C_7H_5O_3Na$. – IR (KBr): $\tilde{\nu}(CO_2)$sym = 1685 cm^{-1}.

The quantitative determination of the ratio of sodium phenoxide to CO_2 in THF and dioxane was carried out using gas volumetric analysis.

FT-IR Measurements (Perkin-Elmer 16 PC FT-IR): The sodium phenoxide–CO_2 complex was suspended in nujole and introduced into a thermocontrolled KBr cuvette. At intervals of 5 K FT-IR spectra were recorded up to 80 °C.

Separation and Quantitative Analysis of Phenol, Salicylic and 4-Hydroxobenzoic Acid with HPLC (Gynkotek): The method was developed by modifying a previously described procedure[18]. Column: Lichrosorb RP-8 (Merck), injection volume: 20 µl, solvent A: water/Lure buffer (95:5), Lure buffer: 0.04 M H_3PO_4, H_3BO_3, CH_3COOH, solvent B: methanol, solvent system: 88% solv. A, 12% solv. B, pH = 3.0, flow rate: 2.0 ml/min, isotherm at 25 °C, programme: isocratic, wavelength: 214 nm.

DTA (Rigaku): 4.5 mg of the sodium phenoxide$-CO_2$ complex were transferred under CO_2 into a measuring cuvette, cooled with liquid nitrogen, and sealed. The heating rate was 5 K min^{-1} and the reference material was Al_2O_3.

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[8] The lattice constants were refined using 20 reflections with 2θ between 15° and 25°. In all structure determinations, Mo-$K\alpha$ radiation (λ = 0.7107Å) and a graphite monochromator were used. All structures were solved by direct methods; all hydrogen atoms were geometrically fixed to the carbon atoms, and the overall refinement method used was full- matrix least-squares on F^2[19]. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-404964, CSD-404965, and CSD-406707, the names of the authors, and the journal citation.

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