

Note

Diverse coordination modes in solvated alkali metal phenolates: The crystal structures of rubidium phenolate · 3 phenol and cesium phenolate · 2 phenol

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Dedicated to Professor Vincenzo Balzani on the occasion of his 70th birthday.

Abstract

Two alkali metal phenolate/phenol complexes are reported. The cations are pseudo-octahedrally coordinated by oxygen atoms and the π -systems of phenolates and solvent phenols. The ratio of phenolate/phenol determines whether the oxygen atom of the phenolate participates in the coordination of the metal. In cesium phenolate · 2 phenol, both phenolate and phenol solvent coordinate the metal via oxygen and the π -system, whereas in rubidium phenolate · 3 phenol, the phenolate oxygen is excluded from coordination and instead linked via hydrogen bonds to the phenol solvent. In both structures, the coordination polyhedra share edges or faces and form infinite chains.

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1. Introduction

In recent years, several systematic studies of alkali metal alkoxides and phenoxides, including theoretical calculations and investigation of crystal structures, have been undertaken to provide insight into the bonding energies and reactivity of these compounds [1–5]. The solid-state structures of alkali metal phenolates (MOPh) are of particular interest as they are the precursors of the Kolbe–Schmitt reaction [6] in which MOPh reacts with CO₂ to form salicylic acid or *para*-hydroxybenzoic acid, depending on the alkali metal (e.g., sodium phenolate produces salicylic acid, whereas larger cations predominately form *para*-hydroxybenzoic acid). The crystal structures of the solvent-free phenolates have been elucidated [3,7] and reveal significant differences within the Na–Cs series that may be responsible for the regioselectivity in the Kolbe–

Schmitt reaction. Recently, studies on the effect of the alkali metals and other cations on the carboxylation of phenolates confirmed the role of the cation, concluding that larger cations obstruct the *ortho*-position on the phenolate and prevent carboxylation in this position [4,5,8]. Few studies have addressed the effect of the cation's coordination sphere and the extended structure on regioselectivity [3].

While attention remains focussed on solvent-free phenolates, the structures of phenol and other solvates might provide additional insight into the regioselectivity of the Kolbe–Schmitt reaction [9]. Thus far, only three MOPh · *n*PhOH structures have been determined: NaOPh · 2PhOH [10], KOPh · 2PhOH, and KOPh · 3PhOH [11]. The structures are significantly different and notably influenced by the identity of the cation, as well as the degree of solvation. Here, we report two phenolate phenol solvates with larger cations, rubidium and cesium. We compare their structures to the known MOPh · *n*PhOH structures and discuss their potential relevance to the Kolbe–Schmitt reaction.

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2. Experimental

2.1. General

All manipulations were conducted under the careful exclusion of air and moisture using standard Schlenk techniques and dried argon. Prior to use, THF was distilled from sodium benzophenone ketyl under argon. Rubidium and cesium metal were purchased from Aldrich and used without further purification. Phenol was sublimed and stored under argon.

2.2. Rubidium phenolate · 3 phenol

A Schlenk vessel was charged with rubidium metal (1 g ampule, 12 mmol) and cooled in ice water. Four equivalents of phenol (4.47 g, 48 mmol) dissolved in 50 ml THF were added dropwise, under vigorous stirring while the mixture was allowed to attain room temperature. The mixture was stirred and heated at 50 °C for 2 h to drive the reaction to completion. Slow evaporation of the solvent yielded colourless needles of the compound. M.p. 144–148 °C (under Ar). IR (CsI, cm^{-1}): 3431.74, 3054.46, 2587.38, 1930.48, 1599.29, 1588.84, 1474.27, 1380.69, 1272.67, 1242.20, 1167.60, 1071.98, 994.30, 888.52, 820.63, 755.06, 693.40, 618.54, 551.70, 531.92, 515.85, 477.85. Metal content (ICP-MS): $^{85}\text{Rb}^+$, 23.5(2)%, $^{133}\text{Cs}^+$, 0.4(3)%.

2.3. Cesium phenolate · 2 phenol

Analogous to rubidium phenolate · 3 phenol, cesium metal (1 g ampule, 7.52 mmol) was reacted with three equivalents of phenol (2.28 g, 24 mmol) dissolved in THF. Slow evaporation of the solvent afforded colourless needles of the compound. M.p. 108–112 °C (under Ar). IR (CsI, cm^{-1}): 3434.96, 3018.80, 2534.60, 1846.76, 1631.99, 1594.24, 1574.22, 1467.98, 1403.55, 1303.31, 1273.30, 1241.92, 1156.55, 1069.96, 987.68, 880.28, 829.07, 774.04, 762.63, 696.54, 617.77, 560.88, 531.00, 515.41, 497.97. Metal content (ICP-MS): $^{85}\text{Rb}^+$, 0.5(2)%, $^{133}\text{Cs}^+$, 41.9(3)%.

2.4. Spectroscopic and other analyses

IR spectra were obtained using an FTIR-2000, Perkin Elmer. Metal content was determined with an ICP mass spectrometer Elan 5000, Sciex/Perkin Elmer. Melting points were determined in sealed capillaries with a Gallenkamp variable heat melting point apparatus at a heating rate of 1 K/min.

2.5. X-ray crystallography

All data were collected with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, graphite monochromator) on a STADI4 diffractometer, Stoe Darmstadt, using the program DIF4 [12]

at 220 K. Initial orientation matrices were determined from at least 20 strong reflections with DIF4. Data were scaled using three periodically measured standard reflections and reduced with REDU4 [13]. Final lattice constants were obtained from selected reflections between 20° and 30° in 2θ . Data were corrected for absorption effects using ψ -scans [14]. Space groups were determined based on intensity statistics and systematic absences. Structures were solved with direct methods using SHELXS-86 [15] and refined with full-matrix least squares/difference Fourier cycles using SHELXS-93 [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

3. Results and discussion

Phenolate/phenol complexes had been predicted from phase diagrams and differential thermoanalysis [17] but only three structures have been determined [10,11]. We embarked on a systematic investigation of higher alkali metal analogues to compare solid-state structures of these complexes and expected to find very similar structures as those observed for potassium. Indeed, $\text{RbOPh} \cdot 3\text{Ph}$ (Fig. 1) is isostructural (but not isomorphous) to the potassium analogue. Crystallographic information is summarized in Table 1 and selected geometric parameters are listed in Table 2.

The metal is pseudo-octahedrally coordinated by five oxygen atoms of solvent phenol (average distance of 3.025 Å) and the π -system of the phenolate anion; the distance to the centre of the phenyl ring is 3.323 Å. The oxygen of the phenolate does not take part in the coordination of the metal. Instead, it forms hydrogen bonds with the phenol oxygens (the average distance $\text{PhO} \cdots \text{O}(\text{H})\text{Ph}$ is 2.602 Å); the phenolate $\cdots \text{HOPh}$ distances are between

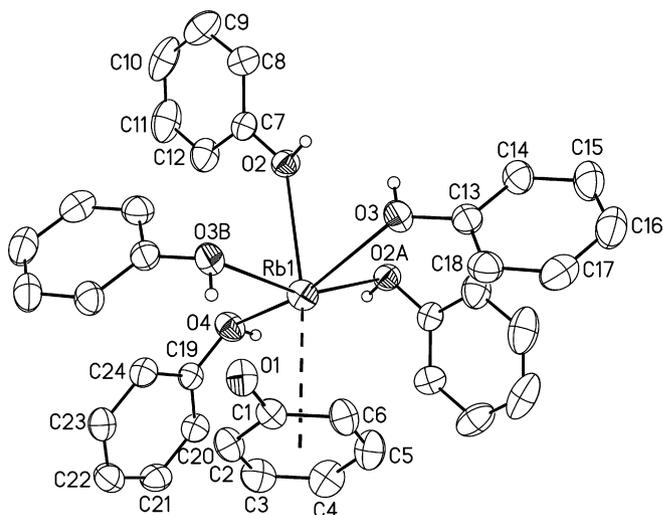


Fig. 1. Coordination sphere of Rb in $\text{RbOPh} \cdot 3\text{Ph}$, with ellipsoids at 30% probability; phenyl hydrogens are omitted for clarity. Symmetry operations, A: $-x + 1, -y + 1, -z + 1$; B: $-x + 1, -y, -z + 1$.

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