



Syntheses and crystal structures of mono-, di- and trinuclear cobalt complexes of a salen type ligand

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ABSTRACT

Three cobalt complexes containing the salen type ligand, bis(salicylidene)-meso-1,2-diphenylethylenediaminato (mdpSal^{2-}), are reported. The complexes differ in nuclearity and include the mononuclear, $\text{Co}(\text{mdpSal})$ (**1**), which contains a Co(II) metal center bound to one mdpSal^{2-} ligand frame in a square planar geometry. The second complex is the dinuclear $[\text{Co}(\text{mdpSal})\text{Cl}]_2$ (**2**) in which both cobalt ions have been oxidized to the +3 oxidation state. The overall geometry of complex **2** is an edge-sharing bioctahedron with the coordination sphere around each cobalt metal center consisting of one mdpSal^{2-} ligand and one Cl^- ion. The shared edge between the Co(III) ions contains two bridging phenolate groups, one from each ligand frame. Complex **3** is a linear, mixed valence, trinuclear species, $[\text{Co}(\text{mdpSal})(\text{OAc})(\mu\text{-OAc})_2\text{Co}]_2$, with the oxidation states of the metal centers assigned as Co(III)–Co(II)–Co(III). The terminal Co(III) centers are equivalent with the central Co(II) lying on the inversion center of the molecule. Each cobalt ion in **3** adopts an octahedral geometry with the terminal Co(III) ions being bound to one mdpSal^{2-} ligand each. All phenolate groups bridge to the central Co(II). The coordination sphere about each metal center in the trinuclear complex is completed by four acetate groups, two of which bind in a μ -fashion bridging from the terminal Co(III) metal centers to the central Co(II). The complexes have been characterized by X-ray crystallography as well as UV–Vis and IR spectroscopy.

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1. Introduction

Organic molecules containing imine groups have been of interest to inorganic chemists for some time. These types of molecules have been shown to be good ligands for transition metals and have found utility in a broad range of applications. Undoubtedly, the Schiff base ligands receiving the most attention have been those classified as Salen type ligands. Ligands categorized in this class are tetradentate, consisting of two imine nitrogen and two phenolic oxygen donors that coordinate in the basal plane of the metal ion, and are readily prepared from the condensation of a salicylaldehyde and a diamine. Factors that have contributed to the widespread and continued interest in Salen type ligands are (a) the initial recognition that metal complexes containing these types of ligands can reversibly bind O_2 [1–4], (b) the similarity between Salen type ligands and heme and hence their use in model complexes [5,6] and finally, (c) the more recent discovery of Salen complexes as efficient chiral catalyst, a field which continues to be at the forefront of research efforts [7–11].

The success of Salen type ligands in coordination compounds is due in part to the ease of which a variety of substituents can be appended to the ligand periphery and the affinity of this donor set for many different metal ions [12–16]. These inherent properties have made this ligand class a unique platform to perform systematic studies on in order to achieve a desired outcome. Indeed, changing one of these two factors has great influence on the characteristics of the coordination complex. For example Jacobsen employed the same Salen type ligand system with both Cr and Mn and found the Cr analogue to be an effective catalyst for the enantioselective ring opening of epoxides while the Mn derivative catalyzes the enantioselective epoxidation of olefins (Fig. 1) [17–19].

Another characteristic of the Salen type ligands, albeit less studied, is their potential to form multinuclear complexes. This feature arises due to the susceptibility of deprotonated phenolic oxygen donors to bind more than one metal ion [20–22]. Interest in homo-dinuclear complexes continues to develop owing to their discovery in such biological systems as the di-nickel containing ureases [23] and the bifunctional enzyme ACS/CODH [24], the di-iron core of the hydroxylase unit of methane monooxygenases [25] and the di-copper hemocyanins [26] to name a few. In addition, homo- and hetero-multinuclear complexes display novel magnetic, structural and redox properties which continue to make them of interest [27–30].

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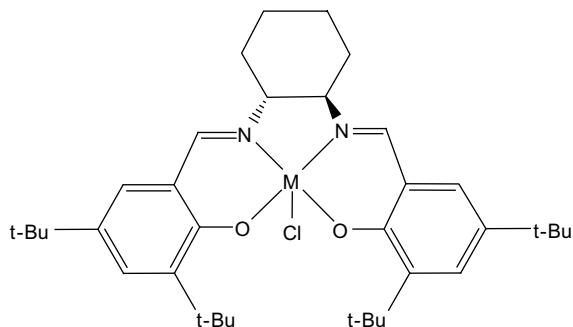


Fig. 1. Salen type ligand employed by Jacobsen et al. M = Cr or Mn.

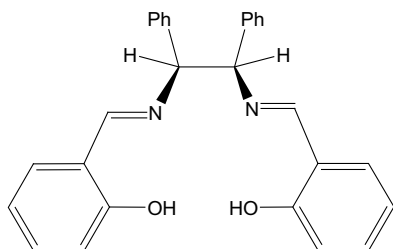


Fig. 2. *N,N'*-Bis(salicylidene)-meso-1,2-diphenylethylenediamine (mdpSalH₂).

We have isolated three new cobalt containing complexes with the Salen type ligand *N,N'*-bis(salicylidene)-meso-1,2-diphenylethylenediamine (mdpSalH₂) (Fig. 2) which differ in nuclearity, namely the mononuclear Co(mdpSal) (**1**), the dinuclear [Co(mdpSal)Cl]₂ (**2**) and the linear, mixed valence, trinuclear species [Co(mdpSal)(OAc)(μ-OAc)]₂Co (**3**). This work describes the synthesis, characterization and crystal structure of each complex, **1–3**.

2. Experimental

2.1. Materials

Salicylaldehyde (98%), meso-1,2-diphenylethylenediamine (98%), Co(OAc)₂·4H₂O and anhydrous solvents were purchased from Sigma–Aldrich Chemical Co. and used without further purification.

2.2. Physical measurements

Infrared spectra were obtained with a Thermolectron, Avatar 330 FT-IR spectrophotometer equipped with a Smart Orbit reflectance insert, diamond window. Absorption spectra were measured on a Hewlett-Packard 8453 diode array spectrophotometer. ¹H spectra were recorded on a Varian 200 MHz spectrometer.

2.3. Preparation of compounds

The ligand, mdpSalH₂, was prepared using a method similar to those used to synthesize other Salen type ligands [31]. The starting materials (salicylaldehyde and meso-1,2-diphenylethylenediamine) were dissolved in a minimum amount of EtOH and added together in a 1:1 ratio. Upon mixing, an immediate bright yellow precipitate formed. The reaction was stirred for 2 h and the solid collected and dried under high vacuum. Yield: 85%. ¹H NMR (CDCl₃, 200 MHz, 25 °C, δ from TMS): 4.75 (s, 2H, ethylene), 6.81 (t, 2H), 6.92 (d, 2H), 7.07 (d, 2H), 7.15 (m, 12H), 8.09 (s, 2H, imine), 13.1

(s, 2H, OH). Selected IR bands: (cm⁻¹) 1620, 1576 (m, ν_{NC}), 1493 (m), 1278 (m), 1052 (m), 758 (s), 701 (s).

2.3.1. Synthesis of Co(mdpSal) (**1**)

A batch of 0.194 g (0.499 mmol) of mdpSalH₂ was suspended in 20 mL of MeOH. After 20 min, 0.124 g (0.449 mmol) of Co(OAc)₂·4H₂O dissolved in 10 mL of MeOH were added to it. Upon addition of the metal, the solution immediately turned red-brown and a bright orange precipitate began to form. The mixture was stirred for 3 h and the solid collected by gravity filtration and dried under high vacuum. Yield: 0.15 g (63%). Selected IR bands: (cm⁻¹) 1599, 1578 (m, ν_{NC}), 1524 (m), 1428 (m), 1146 (m), 757 (s), 701 (s). Electronic absorption spectrum in CH₂Cl₂: λ_{max} (nm) (ε, M⁻¹ cm⁻¹) 415 (10248), 350 (9798), 265 (30580), 240 (40071). Anal. Calc. for C₂₈H₂₂CoN₂O₂: C, 70.44; H, 4.64; N, 5.87. Found: C, 70.30; H, 4.62; N, 5.87%.

2.3.2. Synthesis of [Co(mdpSal)Cl]₂ (**2**)

Complex **1** (0.125 g, 0.262 mmol) was dissolved in CH₂Cl₂ and refluxed. After 30 min, 1 drop of concentrated HCl was added to it. The solution immediately changed from orange to red-orange in color. Slow diffusion of diethyl ether (Et₂O) into the solution resulted in the isolation of **2** as red blocks. Yield: 67 mg (50%). Selected IR bands: (cm⁻¹) 1603, 1597 (m, ν_{NC}), 1443 (m), 1323 (m), 1238 (w), 908 (w), 700 (s). Electronic absorption spectrum in CH₂Cl₂: λ_{max} (nm) (ε, M⁻¹ cm⁻¹) 340 (11193), 250 (43005). Anal. Calc. for C₂₈H₂₂Co₂N₂O₂Cl₂: C, 65.71; H, 4.64; N, 5.38. Found: C, 65.28; H, 4.46; N, 5.30%.

2.3.3. Synthesis of [Co(mdpSal)(OAc)(μ-OAc)]₂Co (**3**)

Complex **3** was isolated as a byproduct from the reaction which resulted in the formation of complex **1**. Whilst complex **1** was filtered off from the reaction mixture, slow evaporation of the methanolic mother liquor afforded isolation of complex **3** as orange microcrystalline solid. The solid was collected and dried under high vacuum for 12 h. Yield: 0.11 g (36%, based on Co). Selected IR bands: (cm⁻¹) 1622 (m), 1601, (s, ν_{NC}), 1548 (m), 1447 (m), 1293 (s), 1206 (w), 907 (m), 739 (s), 701 (s). Electronic absorption spectrum in CH₂Cl₂: λ_{max} (nm) (ε, M⁻¹ cm⁻¹) 400(sh) (10991), 375 (18412), 374 (16402), 300(sh) (24965), 275 (sh) (50805), 240 (124661). Anal. Calc. for C₆₄H₅₆Co₃N₄O₁₂: C, 61.50; H, 4.52; N, 4.48. Found: C, 61.10; H, 4.65; N, 4.47%.

2.4. X-ray data collection and structure solution and refinement

Crystals suitable for X-ray analysis were obtained using the following procedures at room temperature: Red blocks of Co(mdpSal) (**1**) were obtained within 24 h by diffusion of Et₂O into a solution of **1** in CH₂Cl₂. Red blocks of the dietherate of [Co(mdpSal)Cl]₂ (**2**·2Et₂O) were obtained by slow diffusion Et₂O into a solution of **2** in CH₂Cl₂ after 48 h. Slow diffusion of Et₂O into a methanolic solution of [Co(mdpSal)(OAc)(μ-OAc)]₂Co yielded orange needles of **3** as a solvate (**3**·8CH₃OH) within 4 h. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα (λ = 0.71073 Å)) equipped with and Oxford liquid nitrogen cold stream. Suitable crystals were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F² with SHELXTL (Version 6.14) [32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. Hydrogen atoms on oxygen were refined semi-freely using a distance restraint. Crystal data and refinement details are presented in Table 1 for complexes **1–3** while selected

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