Packing polymorphism of dicarbonyl-[2-(phenylamino)pent-3-en-4-onato]rhodium(I)

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ABSTRACT

Depending on the crystallization conditions, the interaction between the rhodium metal centres of the separate [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$] molecular units, as described by the interplanar separation and lateral shift of two of the units, leads to packing polymorphism of [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$], which means the same molecule crystallises in different fashions, resulting in different polymorphs (α and β), with a difference in crystal packing. Six different sets of solid state single crystal data of [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$], show that this complex is polymorphic, forming dinuclear units that either stack in wire-like chains with weak metallophilic rhodium-rhodium interactions (β-polymorph), or with packing of the dinuclear units that does not result in rhodium-rhodium chains (α-polymorph). A DFT study on the inter-molecular interactions in different dinuclear [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$]$_2$ models, using different DFT methods, provides an understanding on a molecular level of the rhodium-rhodium and other inter-molecular interactions between the two separate [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$] molecules in the dinuclear unit.

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1. Introduction

Polymorphism [1] has been defined by McCrone in 1965 as "a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state" [2]. A few years later, Rosenstein and Lamy (1969) simplified the definition to "when a substance can exist in more than one crystalline state it is said to exhibit polymorphism" [3]. Polymorphs are also described as "isomers at the individual crystal level in which the same molecule or salt crystallises in different fashions, which frequently, but not necessarily, result in differences in the space group and the cell dimensions", sometimes leading to different arrangements (packing) of the molecules in the solid state [4]. When polymorphism exists as a result of differences in crystal packing, it is called packing polymorphism. It has been observed that the molecules of different [Rh(β-diketonato)(CO)$_2$] complexes in the solid state, either pack in separate dinuclear [Rh(β-diketonato)(CO)$_2$]$_2$ dimeric units [5–7], while others of these complexes pack in dinuclear units which form extended linear wire-like chains of rhodium atoms [8–11]. The extended metal-metal interactions along the linear chains in the latter case, have been described as resulting from the overlap of the filled d_{z^2} orbitals and the empty p_z orbitals that lie along the direction of the metal-metal axis [12]. Similarly to the latter, it has been shown recently that crystals of the complex [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$] (dicarbonyl-[2-(phenylamino)pent-3-en-4-onato]rhodium(I)) [13] (see Fig. 1), in the solid state also pack in linear chains of consecutive unit cells along the intermolecular rhodium-metal axis in a wire-like structure (called the β-polymorph), while a related molecule of dicarbonyl-(4-((2,6-dichlorophenyl)imino)pent-2-en-2-olato)-rhodium did not show any inter-molecular rhodium-rhodium interaction in the solid state at all [13]. In this contribution we present an additional packing polymorphism (the α-polymorph) of the same [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$] molecule (as in Fig. 1), complemented by a DFT study on the inter-molecular rhodium-rhodium interactions in four different dinuclear [Rh(CH$_3$COCHCN(Ph)CH$_3$)(CO)$_2$]$_2$ models.

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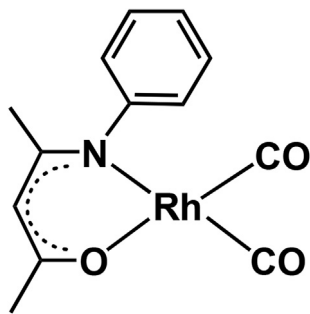
Fig. 1. Structure of [Rh(CH₃COCHCN(Ph)CH₃)(CO)₂].

2. Experimental

2.1. Synthesis

Reagents were obtained from Sigma-Aldrich. Solid reagents employed in preparations were used directly without further purification. Solvents were distilled prior to use. Di-μ-chloro-tetra-carbonyldirhodium(I) was obtained from Sigma-Aldrich.

2.1.1. [CH₃COCHCN(HPh)CH₃]

The ligand [CH₃COCHCN(HPh)CH₃] was synthesised using published methods [14–17] with slight modifications. Acetylacetone (5 g, 5.2 ml) was placed in a round bottom flask outfitted with a condenser for refluxing. Aniline (6.9763 g, 7 ml) and concentrated hydrochloric acid (5 g, 4.3 ml) was added to the flask whilst stirring and the mixture was brought to reflux for 5 h. Diethyl ether was added to the mixture and then placed in the fridge (-5° C). The yellow crystalline precipitate was filtered and washed with cold diethyl ether and recrystallised.

Yield = 50%. ^{1}H NMR: 12.493 ppm (s, O-H); 7.388 ppm—7.114 ppm (m, C₆H₅-N); 5.208 ppm (s, C-H); 2.122 ppm (s, CH₃-CN); 2.014 ppm (s, CH₃-CO).

2.1.2. [Rh(CH₃COCHCN(Ph)CH₃)(CO)₂]

The complex [Rh(CH₃COCHCN(Ph)CH₃)(CO)₂] was synthesised using published methods with slight modifications [18]. The metal, di-μ-chloro-tetracarbonyldirhodium(I) (0.05 g, 0.1286 mmol), was dissolved in methanol (5 ml). The ligand, [CH₃COCHCNHPhCH₃] (0.2572 mmol), also dissolved in methanol (2 ml) was added dropwise during 10 min whilst stirring. The mixture was left to stir for 1 h. The mixture was then extracted with n-hexane until the n-hexane solvent became clear. The solvents were combined and evaporated under reduced pressure. The precipitated solid was collected and recrystallised, either from n-hexane at -5 °C, or from DCM at room temperature (25 °C).

Yield = 78%. ^{1}H NMR: 7.388 ppm—7.061 ppm (m, C₆H₅-N); 5.298 ppm (s, C-H); 2.195 ppm (s, CH₃-CN); 2.141 ppm (s, CH₃-CO). ν_{CO}: 2059 cm^{-1}; 1998 cm^{-1}. UV/Vis (CHCl₃): λ_{max} = 329 nm (ε = 5102 mol^{-1} dm^{+3} cm^{-1}), 265 nm (ε = 6497 mol^{-1} dm^{+3} cm^{-1}).

2.2. Crystal structure analysis

The solid state crystal data of two crystals, obtained under different crystallisation conditions, collected at three different temperatures, for two different crystalline forms of [Rh(CH₃COCHCN(Ph)CH₃)(CO)₂], is presented here. The first crystalline form, labelled the α-polymorph, was obtained from a solution of n-hexane at -5 °C. The second crystalline form, labelled the β-polymorph, was crystallised from a solution of DCM at room temperature. Data for both crystals was collected, both at RT and at 150 K for each of these two

crystalline forms (α- and β-polymorphs), on a Bruker D8 Venture kappa geometry diffractometer, with duo Iμs sources, a Photon 100 CMOS detector and APEX II [19] control software, using Quazar multi-layer optics, and monochromated Mo-Kα radiation, by means of a combination of ϕ and ω scans. An additional set of data for the α-polymorph was collected at 100 K, on a Bruker APEX-II CCD.

Data reduction was performed using SAINT+ [19] and the intensities were corrected for absorption, using SADABS [19]. The five crystal structures were solved by intrinsic phasing, using SHELXTS, and refined by full-matrix least squares, using both SHELXTL+ [20] and SHELXL-2014+ [20]. In the structure refinement, all hydrogen atoms were added in the calculated positions and treated as riding on the atom to which they are attached. All non-hydrogen atoms were refined with anisotropic displacement parameters; all isotropic displacement parameters for hydrogen atoms were calculated as (X × U$_{eq}$) of the atom to which they are attached, where X = 1.5 for the methyl hydrogens, and X = 1.2 for all other hydrogens. Crystal data, data collections, structure solutions and refinement details for all five crystal structures, are available in the CIFs (with CCDC deposit numbers 1548178, 1558071, 1571132, 1571133 and 1571134).

2.3. Theoretical approach

Density functional theory (DFT) calculations of this study were performed with the hybrid B3LYP [21,22] functional, as implemented in the Gaussian 09 program package [23]. Geometries of the neutral complexes were optimised in the gas phase, using the 6-311G(d,p) basis set on all atoms except rhodium, for which the def2tzvpp [24] (valens electrons) and SDD (core electrons) basis set was used. These B3LYP optimised gas phase structures were used to further conduct a natural bond orbital (NBO) analysis (using the NBO 3.1 module [25] in Gaussian 09), a fragment analysis, as well as an electronic density analysis (using Bader's quantum theory of atoms in molecules (QTAIM) [26—28], as implemented in ADF2013 [29—31]), at the same level of theory.

The single molecular unit of complex [Rh(CH₃COCHCN(Ph)CH₃)(CO)₂] was optimised by calculation, as well as the [Rh(CH₃COCHCN(Ph)CH₃)(CO)₂]₂ dimeric unit. Further additional single point calculations were done on the coordinates of such a dinuclear unit which were obtained from the solid state crystal structure data of this study (α-polymorph at 150 K), as well as on two additional dinuclear models, calculated on the coordinates of a dinuclear unit obtained from the solid state crystal structure data of a previous study (β-polymorph at 100 K), as described in Section 3.2.2. The coordinates of the DFT calculations are given in the Supporting Information.

3. Results and discussion

3.1. X-ray structure

In this section, crystallographic results are presented of the solid state crystal data of two polymorphs of complex [Rh(CH₃COCHCN(Ph)CH₃)(CO)₂]; see Table 1 and Table 2 (column 2—6). Data for each crystalline structure was repeatedly collected at decreasing temperatures, to determine whether temperature would transform the structure of each polymorph. The two structures were labelled the α-polymorph (with space group P 2₁/n, data collected at 298 K, 150 K and 100 K), as well as the β-polymorph (with space group I2/a, data collected at 298 K and 150 K). These experimental results were then compared to a previously published structure [13] and packing of the same complex (β-polymorph with space group I2/a, data collected at 100 K); see Table 2 (last column of the β-polymorphs). Crystals suitable for X-ray diffraction were obtained by slow evaporation from