Synthesis and Characterization of Two Isostructural POCOP Ni(II) Pincer Complexes Containing Fluorothiophenolate Ligands: \[ \text{[Ni(SC}_6\text{F}_4-4\text{H})(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})-2,6-(\text{OPr}_2^i)_2)] \] and \[ \text{[Ni(SC}_6\text{F}_5)(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})-2,6-(\text{OPr}_2^i)_2)] \]

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Abstract: Among their many applications, metal pincer complexes are of interest for their properties as catalysts in cross-coupling reactions. Pincer ligands exhibit tridentate coordination to the metal center and occupy the meridional positions forming two chelate rings. The two Ni(II) POCOP pincer complexes with a fluorothiophenolate ligand reported herein, with formulas \([\text{Ni(SC}_6\text{F}_4-4\text{H})(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})-2,6-(\text{OPr}_2^i)_2)]\) (2) and \([\text{Ni(SC}_6\text{F}_5)(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})-2,6-(\text{OPr}_2^i)_2)]\) (3), are isostructural. Additionally, they are prepared in a facile manner from the chloride compound \([\text{NiCl}(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})-2,6-(\text{OPr}_2^i)_2)]\). The complexes exhibited slightly distorted square planar geometries around the metal. The fluorothiophenolate ligands are responsible of the C—H···F, C—F···π and C=O···π interactions that contribute to stabilize the crystal structure arrays.

Keywords: crystal structure; fluorothiophenolate; POCOP ligand; pincer compounds; catalysis; catalyst

1. Introduction

In general, pincer complexes are constituted by an anionic chelating tridentate ligand coordinated in a meridional fashion, the anionic position is coordinated to the metal center by a negatively charged atom, typically a carbon atom of the aryl ring [1,2]. While the other positions are occupied by linkers of the same ligand including donor atoms such as N, P, O, S or Se, located in the pendant arms at the ortho positions to the carbon atom [3]. These characteristics provide stability and play a key role on the reactivity of the complexes they form. These properties, in combination with the mere variation of the metal center, are responsible for the wide variety of applications that pincer compounds have found in different areas of chemistry, this being particularly true in the case of catalysis [4,5].

Over the last years, our research group has focused on the design, synthesis and use of pincer-type ligands and their transition metal complexes [6–8], mainly due to the versatility of applications that they may have in different areas such as catalysis [9,10], materials [11], and medicine [12,13]. Resorcinol-based POCOP-type pincer complexes of group 10 adopt a square planar geometry [14,15]. Traditionally, complexes of these transition metals have been used as efficient catalysts in C–C cross-coupling reactions, which are one of the most important kinds of catalytic reactions to produce carbon–carbon bonds. These reactions have been traditionally catalyzed by Pd(II) species, however in recent years research has
been focused in the potential use of their analogous nickel compounds. Thus, given the aforementioned properties of pincer complexes, Ni(II) pincer compounds have been considered as a suitable alternative for this kind of couplings [16]. Among the pincer complexes, phosphinite POCOP pincer ligands and their complexes have proved to be very valuable, since they exhibit similar and often enhanced reactivity when compared to their phosphine counterparts and are easily synthesized from the direct reaction of resorcinol with a given chlorophosphine. The simplicity of this procedure allows by careful selection of a resorcinol derivative to produce pincer ligands substituted in the 3-position of the aryl ring, giving entrance to the production of non-symmetric pincer ligands and their complexes in a rather simple form [5]. Thus, following our continuous interest in the design of new pincer ligands, their complexes, and potential applications as well as our long-standing interest in the use of fluorothiophenolate moieties to fine tune both electronics and steric in a given compound [17,18], we would like to present our findings in the synthesis, characterization and structural analysis of the two non-symmetric Ni(II)-POCOP pincer complexes [Ni(SC\(_{6}\)F\(_{4}\)-4-H)]\(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O}-2,6-(\text{OP}^\text{Pr}_2)_2)\] (2) and [Ni(SC\(_{6}\)F\(_{5}\)]\(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O}-2,6-(\text{OP}^\text{Pr}_2)_2)\] (3).

2. Results and Discussion

The title complexes were obtained in good yields through metathetical reaction between the parent Ni(II)-POCOP pincer complex and the corresponding thiolate lead salt according to Scheme 1. The POCOP ligand L1 was produced from the direct reaction of 2,4-dihydroxyacetophenone with CIP\(^{\text{Pr}2}\) in a 1:2 molar ratio using and slight excess of triethylamine as base. Further, the Ni(II)-POCOP pincer compound [NiCl\(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})\)-2-6-(OP\(^{\text{Pr}2}\))\] (1) was obtained from the reaction of NiCl\(_2\)-6 H\(_2\)O in refluxing toluene [7]. Finally, the POCOP pincer complexes including the fluorothiophenolate ligands [Ni(SC\(_{6}\)F\(_{4}\)-4-H)]\(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})\)-2,6-(OP\(^{\text{Pr}2}\))\] (2) and [Ni(SC\(_{6}\)F\(_{5}\)]\(\text{C}_6\text{H}_2-3-(\text{C}_2\text{H}_3\text{O})\)-2,6-(OP\(^{\text{Pr}2}\))\] (3) were prepared by metathesis reactions of the parent complex 1 with the lead salts of the corresponding thiophenolates ([Pb(SC\(_{6}\)F\(_{4}\)-4-H)] and [Pb(SC\(_{6}\)F\(_{5}\)]) in both cases, adequate crystals were obtained by slow evaporation of CH\(_2\)Cl\(_2\) solutions of 2 and 3. The two pincer complexes present the pincer ligand with a methylketone fragment in the 3-position of the phenyl ring. Both compounds crystallized in the centrosymmetric space group P2\(_1\)/n with very similar unit cell values (Table 1), intermolecular interactions and packing patterns, these characteristics suggesting isostructurality among the crystal structures. The asymmetric units are consistent of one molecule of the complex and four by unit cell. The coordination geometry around the metal centers Ni(II) in compounds 2 and 3 can be described as a slightly distorted square planar, as shown by the angles around the central atom that are different to 90° (Tables 2 and 3). The deviation from the best plane formed by coordination sphere (Ni1, S3, P1, C2 and P2 atoms) are of r.m.s. = 0.054 and 0.062 Å for complexes 2 and 3, respectively. The bond lengths and angles are similar in both complexes and the molecular structures including atom labels are shown in Figure 1. As expected, the POCOP ligands coordinate to the nickel center in a tridentate fashion via two phosphorus atoms (P1, P2) and one carbon (C2) atom, the ligand forming two chelating five-member rings (Ni–P–O–C–C) with bite angles P1–Ni1–C2 and P2–Ni1–C2 with values of 81.96 (14)° and 82.12 (14)° for complex 2, and 81.98 (8)° and 82.13 (8)° for complex 3. The chelate rings are near to coplanarity with the phenyl ring since the dihedral angles between the mean planes of the rings present values of 2.75 and 2.32° in complex 2, and of 1.84 and 1.48° in complex 3. The bond lengths of the coordinated pincer ligand are similar to other previously reported POCOP pincer complexes [19,20] (Tables 2 and 3).

Completing the coordination sphere around the Ni(II) atoms one thiophenolate ligand (S3), 2,3,5,6-tetrafluorothiophenolate ion (\(^\text{SC}_6\text{F}_4\)-4-H) in complex 2, and 2,3,4,5,6-pentafluoro-thiophenolate ion (\(^\text{SC}_6\text{F}_5\)) in complex 3. The fluorothiophenolate ligands exhibit an orientation near to perpendicularity with the plane formed with the square plane geometry, having dihedral angles between the mean planes of 79.81 (16)° and 76.26 (8)° for compounds 2 and 3, respectively. The Ni1–S3 bond lengths are of 2.2054 (14) and
2.2039 (9) Å with Ni1–S3–C21 angles of 112.37 (17) and 113.61 (10)° for 2 and 3, respectively. The orientation of the thiolate ligand promotes the formation of intramolecular weak hydrogen bond interactions of the type C–H⋯π between the methine (C12–H12) of one of the isopropyls and the fluorothiophenolate group (C21–C26) with distances of 3.095 Å in 2 and of 3.179 Å in 3. Intramolecular C–H⋯S weak interactions between one methyl of the ligands and the sulfur atom as acceptor [C19–H19C⋯S3, C19–H19B⋯S3] (Tables 4 and 5) are also observed.

Table 1. Crystallographic experimental details for (2) and (3).

| Crystal data | (2) CCDC 2142038 | (3) CCDC 2142039 |
|--------------|------------------|------------------|
| Chemical formula | C_{26}H_{34}F_{4}NiO_{3}P_{2}S | C_{26}H_{33}F_{5}NiO_{3}P_{2}S |
| Mr | 623.24 | 641.23 |
| Crystal system, space group | Monoclinic, P21/n | Monoclinic, P21/n |
| Temperature (K) | 151 | 150 |
| a, b, c (Å) | 8.8138 (11), 10.0715 (13), 31.860 (4) | 8.8159 (3), 10.1816 (3), 31.9637 (12) |
| β (°) | 97.397 (4) | 96.109 (2) |
| V (Å³) | 2804.6 (6) | 2852.77 (17) |
| Radiation type | Mo Kα | Mo Kα |
| μ (mm⁻¹) | 0.93 | 0.93 |
| Crystal size (mm) | 0.29 × 0.21 × 0.15 | 0.58 × 0.22 × 0.09 |
| Data collection | Bruker D8 Venture κ geometry diffractometer 208039-1 | Bruker Smart Apex CCD diffractometer 01-670-03 |
| Absorption correction | Analytical [21] | Analytical [21] |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 39113, 6919, 5212 | 38524, 6810, 5292 |
| Rint | 0.080 | 0.080 |
| (sin θ/λ)max (Å⁻¹) | 0.667 | 0.658 |
| Refinement | H-atom parameters constrained | H-atom parameters constrained |
| R[F² > 2σ(F²)], wR(F²), S | 0.069, 0.179, 1.11 | 0.048, 0.099, 1.09 |
| No. of reflections | 6919 | 6810 |
| No. of parameters | 343 | 352 |
| H-atom treatment | w = 1/[2(Fo²) + (0.0516P)² + 13.4197P] where P = (Fo² + 2Fc²)/3 | H-atom parameters constrained |
| ∆ρ_{max}, ∆ρ_{min} (e Å⁻³) | 1.78, -0.60 | 0.70, -0.34 |

Computer programs: APEX2 v2014.1-1 [22], APEX2 v2012.10.0 [22], SAINT V8.34A [22], SAINT V8.27B [22], SHELSX2012 [23], SHEXL2014/7 [24], DIAMOND [25], pubICIF [26].

Table 2. Selected geometric parameters (Å, °) for (2).

| Ni1–C2 | 1.898 (4) |
| Ni1–P2 | 2.1524 (13) |
| C2–Ni1–P2 | 82.12 (14) |
| C2–Ni1–P1 | 81.95 (14) |
| P2–Ni1–P1 | 163.94 (5) |

Table 3. Selected geometric parameters (Å, °) for (3).

| Ni1–C2 | 1.902 (3) |
| Ni1–P2 | 2.1547 (8) |
| C2–Ni1–P2 | 82.13 (8) |
| C2–Ni1–P1 | 81.98 (9) |
| P2–Ni1–P1 | 164.09 (3) |
Scheme 1. General synthesis of pincer complexes (2) and (3).

Figure 1. The molecular structure of compounds (2) and (3), showing the atom labelling schemes. Displacement ellipsoids are drawn at 40% probability level. The intramolecular interactions are drawing as dashed lines.
Table 4. Hydrogen-bond geometry (Å, °) for (2).

| D–H···A | D–H | H···A | D···A | D–H···A |
|---------|-----|------|-------|---------|
| C8–H8B···F2 i | 0.98 | 2.50 | 3.352 (6) | 145 |
| C10–H10A···O3 ii | 0.98 | 2.47 | 3.418 (7) | 163 |
| C10–H10C···F4 | 0.98 | 2.53 | 3.373 (7) | 144 |
| C13–H13C···F1 | 0.98 | 2.50 | 3.307 (7) | 140 |
| C18–H18···O2 iii | 1.00 | 2.64 | 3.615 (6) | 164 |
| C19–H19C···S3 | 0.98 | 2.95 | 3.740 (5) | 138 |
| C20–H20B···F1 | 0.98 | 2.59 | 3.572 (7) | 176 |

Symmetry codes: (i) −x + 1/2, y + 1/2, −z + 3/2; (ii) x, y; (iii) −x + 1, −y + 2, −z + 1.

Table 5. Hydrogen-bond geometry (Å, °) for (3).

| D–H···A | D–H | H···A | D···A | D–H···A |
|---------|-----|------|-------|---------|
| C8–H8C···F2 i | 0.98 | 2.49 | 3.312 (4) | 141 |
| C9–H9···F2 ii | 1.00 | 2.62 | 3.476 (3) | 144 |
| C10–H10A···O3 iii | 0.98 | 2.52 | 3.458 (4) | 160 |
| C10–H10B···F4 | 0.98 | 2.52 | 3.394 (4) | 149 |
| C13–H13B···F1 | 0.98 | 2.59 | 3.325 (4) | 132 |
| C19–H19B···S3 | 0.98 | 2.98 | 3.745 (3) | 136 |

Symmetry codes: (i) −x + 3/2, y − 1/2, −z + 1/2; (ii) x + 1, y, z; (iii) x, y + 1, z.

Being both complexes isostructural the supramolecular arrangements are similar in both compounds. The presence of the fluorothiophenolate moieties give place to C–H···F, C–F···π and C=O···π interactions. Additionally, two lone pair-π interactions (lp-π) were identified [27], the C7=O3···Cg(C21–C26) interaction is formed by the carbonyl and the corresponding fluorothiophenolate group. The interaction exhibits a O···centroid distance of 3.368 (5) Å in complex 2 and of 3.347 (3) Å in complex 3 (−1 + x, 1 + y, z; 1 + x, −1 + y, z), these interactions generate one dimensional chains along the (110) direction (Figure 2). The other lp-π interactions is formed between the F4 atom of the thiophenolate ligand and the phenyl ring (C1–C6) of the pincer ligand, the interactions F···Cg showed distance values of 3.410 (3) and 3.407 (2) Å for complexes 2 and 3 (x, −1 + y, z; x, 1 + y, z), respectively, the interaction is extended along the (010) direction producing linear chains (Figure 3). The supramolecular networks are complemented with C10—H10A···O3=C7 interactions between a methyl and the ketone fragments. The combination of the two lp-π interactions give place to a supramolecular layer parallel to the (110) plane as shown in Figure 4.

Figure 2. Fragment of the structure of compound (2) showing the formation of C7=O3···Cg(C21–C26) interaction (dashed lines). The hydrogen atoms have been omitted for clarity.

The array exhibits two C–H···F interactions (C9–H9···F2 and C11–H11A···F1) between one isopropyl and the fluorothiophenolate, forming an eight-membered cycle motif that is extended along the (100) direction forming chains (Figure 5). Additionally, a centrosymmetric eight-member cycle motif is also identified and is formed by the C18–H18···O2 interaction, giving place to a dimer, these dimers are kept together by the C8–H8B···F2 interaction.
interaction giving place to a bidimensional array parallel to the (101) plane (Figure 6). The C9–H9···F2 and C11–H11A···F1, C18–H18···O2 interactions interlink the layers formed by the lp-π interactions (Figure 4) producing a three-dimensional crystal arrangement.

**Figure 3.** Representation of the chains formed by the F4···Cg(C1–26) and C10–H10A···O3=C7 interactions. The H atoms not involved in these interactions have been omitted for clarity.

**Figure 4.** The molecular packing of compound (2) showing the formation of C7=O3···Cg(C21–C26) and F4···Cg(C1–26) interactions parallel to the (110) plane. The hydrogen atoms are omitted.

**Figure 5.** View of the linear array along the (100) direction due the C9–H9···F2 and C11–H11A···F1 interactions. Only the hydrogen atoms that participle in the interactions are drawn.
Figure 6. Fragment of the molecular packing showing the C18–H18⋯O2 and C8–H8B⋯F2 interactions (dashed lines) forming a layer arrangement parallel to the (101) plane, H atoms not involved in these interactions have been omitted for clarity.

The structural analysis of the isostructural Ni(II)-POCOP pincer compounds show that the inclusion of the fluorothiophenolate ligands, generate interactions like C–H⋯F, C–F⋯π and C=O⋯π that contribute to the stabilization of the crystal packing. The presence of these interactions could contribute to modify the properties so can be used in catalyst, medicine, or material sciences to produce MOFs.

3. Materials and Methods

3.1. General

All chemical reagents were obtained commercially and used as received without further purification. Melting points were recorded on a Mel-Temp II apparatus and are reported without correction. NMR spectra were recorded on a Bruker-Avance 300 MHz spectrometer, the $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra were recorded at 300, 75.6 and 121.7 MHz, respectively. Chemical shifts are reported in p.p.m. (δ) relative to the chemical shift of the residual solvent (CDCl$_3$) for $^1$H and $^{13}$C{$^1$H}. $^{31}$P{$^1$H} NMR spectra were recorded with complete proton decoupling using 85% H$_3$PO$_4$ as an external standard.

Elemental analyses were performed in a Thermo Scientific (Waltham, MA, USA) Flash 2000 elemental analyzer, using a Mettler Toledo XP6 Automated-S Microbalance and sulfanilamide as standard (Thermo Scientific BN 217826, attained values N = 16.40%, C = 41.91%, H = 4.65%, S = 18.63%; certified values N = 16.26%, C = 41.81%, H = 4.71%, S = 18.62%). MS-DART experiments were recorded on a Jeol AccuTOF JMS-T100LC mass spectrometer.

3.2. Synthesis of the Ligand [C$_6$H$_4$-4-(C$_2$H$_3$O)-1-3-(OP$_{i}$Pr)$_2$] (L1)

A Schlenk flask was charged with 2,4-dihydroxyacetophenone (1.3 mmol), Et$_3$N (3.3 mmol) and 20 mL of dry THF. The resulting mixture was stirred for 30 min at room temperature and then a solution of ClP$_{i}$Pr$_2$ (2.6 mmol) in 5 mL of THF was added dropwise. The mixture was then set to reflux for 12 h and allowed to cool down to room temperature.
before filtered via cannula. The solvent was removed from the filtrate under vacuum to afford ligand L1 as a colorless viscous oil. Identity and purity of the ligand was assessed by $^{31}$P$^{[1]}$H NMR. Thus, this compound was used in the next step without further purification. Yield: 80%. $^{31}$P$^{[1]}$H NMR (122 MHz, CDCl$_3$): $\delta$ 148.2 and 148.8 p.p.m.

3.3. Synthesis of Complex $[\text{NiCl}(_2\text{C}_6\text{H}_2-3,3'-\text{O})_{2}]$ (1)

A solution of ligand L1 (0.5 mmol) in toluene (10 mL) was added dropwise to a suspension of NiCl$_2$·6H$_2$O (0.5 mmol) in toluene (20 mL). The resulting mixture was set to reflux for 16 h. After this time, the solvent was removed under vacuum and the crude product purified by column chromatography (hexanes/AcOEt 8:2) to afford the pure complex 1 as a yellow microcrystalline solid. Yield: 68%, 0.162 g; m.p. 136–138 °C. 

Carbon-bound H atoms were positioned geometrically and included as riding atoms, with $U_{iso}(H)$ values of 1.5U$_{eq}$(C) for methyl H, and C–H = 0.98 Å with $U_{iso}$(H) values of 1.2U$_{eq}$(C) for methine. For more information about the structures of compounds 2 and 3, please refer to Supplementary Materials, as the picture shows.

3.4. General Procedure for Synthesis of Complexes 2 and 3

To a solution of complex 1 (0.088 mmol) in CH$_2$Cl$_2$ (10 mL), a solution of either [Pb(SC$_2$F$_4$)$_2$] (0.44 mmol) in acetone (20 mL) was added dropwise under stirring. The resulting red-brick solution was stirred overnight. After this time the resulting reaction mixture was filtered through a short plug of Celite® to remove the PbCl$_2$ and the solvent was removed under vacuum and the residue recrystallized from CH$_2$Cl$_2$ affording in both cases yellow crystals, that were suitable for the X-ray diffraction analysis.

3.4.1. $[\text{Ni}(_2\text{C}_6\text{H}_2-3,3'-\text{O})_{2}]$ (2)

Yield: 93%, 0.051 g; m.p. 131–134 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.58 (d, 1H, $J_{1H,H} = 8.5$ Hz), 6.65 (m, 1H), 6.46 (d, 1H, $J_{1H,H} = 8.5$ Hz), 2.48 (s, 3H, CH$_3$), 2.01–2.15 (m, 4H, CH). $^{31}$P NMR (122 MHz, CDCl$_3$): $\delta$ 194.21 (d, (AB)$_2$P$_{PP}$ = 293 Hz, 1P), 191.05 (d, (AB)$_2$P$_{PP}$ = 293 Hz, 1P). $^{19}$F NMR (283 MHz, CDCl$_3$): $\delta$ = −130.99–131.16 (m, o-F), −140.81–141.00 (m, m-F). MS (DART) m/z: 638 [(100%) M$^+$H]$^*$. Anal. Calcd (%) for C$_{26}$H$_3$F$_3$NiO$_3$P$_2$: C, 50.11; H, 5.50. Found: C, 50.13; H, 5.52.

3.4.2. $[\text{Ni}(_2\text{C}_6\text{H}_2-3,3'-\text{O})_{2}]$ (3)

Yield: 90%, 0.050 g; m.p. 145–149 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.58 (d, 1H, $J_{1H,H} = 8.5$ Hz), 6.46 (d, 1H, $J_{1H,H} = 8.5$ Hz), 2.48 (s, 3H, CH$_3$), 1.99–2.16 (m, 4H, CH), 1.13–1.36 (m, 24H, CH$_2$). $^{31}$P NMR (122 MHz, CDCl$_3$): $\delta$ 194.38 (d, (AB)$_2$P$_{PP}$ = 292 Hz, 1P), 191.22 (d, (AB)$_2$P$_{PP}$ = 292 Hz, 1P). $^{19}$F NMR (283 MHz, CDCl$_3$): $\delta$ = −161.08–161.35 (m, p-F), −163.61–163.95 (m, m-F). MS (DART) m/z: 642 [(100%) M$^+$H]$^*$. Anal. Calcd (%) for C$_{26}$H$_3$F$_3$NiO$_3$P$_2$: C, 48.70; H, 5.19. Found: C, 48.69; H, 5.17.

3.5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Carbon-bound H atoms were positioned geometrically and included as riding atoms, with C–H = 0.98 Å with $U_{iso}$(H) values of 1.5U$_{eq}$(C) for methyl H, and C–H = 0.98 Å and 1.00 Å with $U_{iso}$(H) values of 1.2U$_{eq}$(C) for methine. For more information about the structures of compounds 2 and 3, please refer to Supplementary Materials, as the picture shows.

4. Conclusions

Thus, in conclusion, we have provided a facile procedure for the synthesis of two Ni(II) pincer complexes including fluorinated thiolates on their structures. The complexes
were fully characterized both in solution and solid state. Further analysis in the solid state revealed some interesting features that can be useful for the further development of these species and potential uses in catalysis, medicinal chemistry and materials sciences, some of these possibilities being currently explored in our laboratories.

Supplementary Materials: The following supporting information can be downloaded. Supplementary data for complexes (2) and (3) has been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk (accessed on 21 January 2022), quoting the deposition numbers CCDC 2142038-2142039.

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