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[(2-oxidoethyl)iminomethyl]phenolato-
 κ 3O,N,O'molybdenum(VI)**

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Polymorph of {2-[(2-hydroxyethyl)-iminomethyl]phenolato- κ O}dioxido-{2-[(2-oxidoethyl)iminomethyl]-phenolato- κ 3O,N,O'}molybdenum(VI)

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Abstract

A second polymorphic form (form I) of the previously reported Dioxo-(N-salicylidene-2-aminoethanolato-N,O,O')-(2-N-hydroxyethyliminomethyl) phenolato-O)-molybdenum(VI) (form II), C₁₈H₁₉MoN₂O₆, is presented. The title polymorph structure differs from the previously reported by the fact that the asymmetric unit contains three molecules linked by O—H···O hydrogen bonds. These trimeric units are further linked through O—H···O hydrogen bonds to form a chain parallel to the [-1 1 1] direction. As for the previous polymorph, each molecule is built up from an MoO₂²⁺ cation surrounded by a three-coordinating ONO ligand (O⁽⁻⁾C₆H₄—CH=NCH₂CH₂O⁽⁻⁾) and weakly coordinated by a second zwitterionic ligand O⁽⁻⁾C₆H₄CH=N⁽⁺⁾HC₂H₄OH. All complexes are chiral with the absolute configuration at the Mo being C, or A. The main difference between the two polymorphs results from the alternance of the chirality at Mo within the chain.

1. Introduction

2. Experimental

2.1. Synthesis and crystallization

Less than two equivalents of HOCH₂CH₂NH₂ (0.3 mL, 4.97 mmol) were added to an ethanol solution (10 mL) of one equivalent of MoO₂(sal)₂ (0.92 g, 2.48 mmol) previously synthesized following a literature procedure (Yamanouchi & Yamada, 1974). The mixture was maintained under reflux for 30 minutes. The white precipitate that formed was separated. The solution is subsequently cooled to room temperature and was left standing in air. Evaporation of the filtrate gave air-stable yellow crystals of the title compound, Mo(O)₂(1.2-OC₆H₄CH=NC₂H₄—O)(1.2-O⁽⁻⁾C₆H₄CH=N⁽⁺⁾HC₂H₄OH). The IR spectrum in KBr pellets of the yellow crystals showed no visible difference with the compound synthesized earlier (Głowiak *et al.*, 2003)

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms attached to C atoms and O atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.97 Å (methylene) and O—H = 0.84 Å with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C).

The two polymorphs have the same P $\bar{1}$ space group but no relation between them could be found, moreover the simulated powder patterns using PLATON (Spek, 2003) are different (Fig. 5).

3. Results and discussion

Molybdenum oxo-complexes bearing polydentate ligands are known to be efficient epoxidation catalysts (Bruno *et al.*, 2006, Herrmann *et al.*, 2002, Martos-Calvente *et al.*, 2004, Most *et al.*, 2002, Valente *et al.*, 2001, Wong *et al.*, 1998,

Zhao *et al.*, 2003, Zhou *et al.*, 2004, Sobczak & Ziolkowski, 2003). Thus, since we were interested to investigate the catalytic activity of Mo(VI) complexes linked to tridentate ligands, we have synthesized and structurally characterized the title compound (**I**).

Reaction of $\text{MoO}_2(\text{sal})_2$ with ethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$) under the described conditions (Głowiak *et al.*, 2003) led to a new polymorphic crystalline structure of $\text{Mo}(\text{O})_2(1,2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_2\text{H}_4\text{O})(1,2\text{-O}^{\ominus}\text{C}_6\text{H}_4\text{CH}=\text{N}^{\oplus}\text{HC}_2\text{H}_4\text{OH})$ with three crystallographically independent molecules per unit cell. The two polymorphs crystallize in triclinic $\bar{P}1$ space group with different cell parameters [(**I**) $a = 10.096 \text{ \AA}$, $b = 13.565 \text{ \AA}$, $c = 21.879 \text{ \AA}$, $\alpha = 81.68^\circ$, $\beta = 86.40^\circ$, $\gamma = 71.41^\circ$, $V = 2810.9 \text{ \AA}^3$, $Z = 6$; (**II**) (Głowiak *et al.*, 2003) $a = 8.483 \text{ \AA}$, $b = 10.187 \text{ \AA}$, $c = 11.034 \text{ \AA}$, $\alpha = 105.26^\circ$, $\beta = 95.29^\circ$, $\gamma = 95.10^\circ$, $V = 909.6 \text{ \AA}^3$, $Z = 2$].

For both (**I**) and (**II**) the molecule is based on a MoO_2^{2+} cation surrounded by a doubly charged anionic ONO tridentate ligand ($\text{O}^{\ominus}\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{O}^{\ominus}$) and weakly O-coordinated to a zwitterionic ligand $\text{O}^{\ominus}\text{C}_6\text{H}_4\text{CH}=\text{N}^{\oplus}\text{HC}_2\text{H}_4\text{OH}$ (Fig. 1). The zwitterionic form is stabilized by intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the $\text{N}^{\oplus}\text{H}$ group and the O atom within the same ligand linked to the Mo. A second weak interaction may be noted between the same $\text{N}^{\oplus}\text{H}$ and one of the O atom of the tridentate ligand (O13, O23 or O33, Table 1).

All the crystallographically independent complexes are chiral at the Mo, and the absolute configuration of each Mo could be determined to be *C* (clockwise) or *A* (anticlockwise) (Fig. 2) using the official nomenclature rules for such compounds (Brown *et al.*, 1975; Hartung *et al.*, 2006).

The title polymorph structure (**I**) differs from structure (**II**) by the fact that the asymmetric unit of (**I**) contains three molecules linked by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 1) involving the hydroxyl O atom of the zwitterionic ligand of one molecule to an oxo O atom attached to Mo atom of another molecule. These trimeric units are further linked through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds of the same type to form a chain parallel to the $[-1\ 1\ 1]$ direction (Fig. 3).

Although the chirality is different for each molecule, they have roughly the same conformation. Indeed an overlay analyses calculated using the structure matching software (Watkin *et al.*, 2003; Collins *et al.*, 2006) shows that the three molecules could be superimposed (Fig. 4, Table 2). A similar overlay analyses of the two polymorphs indicates that the largest deviation occurred for the dangling hydroxyl O atom (Fig. 4) not coordinated to the molybdenum atom and involved in hydrogen bonding which is not surprising owing to the different packings observed in both isomers.

However it is worth to point out that in compound (**II**), the chain is formed from complexes having the same configuration *C* (or *A*) whereas in the title compound (**I**) the chain is built up from trimeric units linked by translation to form infinite $(\text{C}, \text{A}, \text{C})_n$ [or $(\text{A}, \text{C}, \text{A})_n$] chains (Fig. 2).

As observed in polymorph (**II**), there are also intramolecular hydrogen bonds between the dangling NH (N12, N22 or N32) group of the monodentate ligand and the O atom (O15, O25 or O35) within the same ligand. Moreover the position of the dangling $\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$ chain over the chelating ligand is certainly induced by a second weak $\text{N}-\text{H}\cdots\text{O}$ interaction involving one of the O atom (O13, O23 or O33) of the tridentate ligand (Table 1).

4. Synthesis and crystallization

Less than two equivalents of $\text{HOCH}_2\text{CH}_2\text{NH}_2$ (0.3 mL, 4.97 mmol) were added to an ethanol solution (10 mL) of one equivalent of $\text{MoO}_2(\text{sal})_2$ (0.92 g, 2.48 mmol) previously synthesized following a literature procedure (Yamanouchi & Yamada, 1974). The mixture was maintained under reflux for 30 minutes. The white precipitate that formed was separated. The solution is subsequently cooled to room temperature and was left standing in air. Evaporation of the filtrate gave air-stable yellow crystals of the title compound, $\text{Mo}(\text{O})_2(1,2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_2\text{H}_4\text{O})(1,2\text{-O}^{\ominus}\text{C}_6\text{H}_4\text{CH}=\text{N}^{\oplus}\text{HC}_2\text{H}_4\text{OH})$. The IR spectrum in KBr pellets of the yellow crystals showed no visible difference with the compound synthesized earlier (Głowiak *et al.*, 2003)

5. Refinement

All H atoms attached to C atoms and O atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.97 Å (methylene) and O—H = 0.84 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$.

The two polymorphs have the same $P\bar{1}$ space group but no relation between them could be found, moreover the simulated powder patterns using PLATON (Spek, 2003) are different (Fig. 5).

Table 1

Experimental details

Crystal data	
Chemical formula	$\text{C}_{18}\text{H}_{20}\text{MoN}_2\text{O}_6$
M_r	456.30
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	180
a, b, c (Å)	10.0953 (5), 13.5645 (8), 21.8864 (14)
α, β, γ (°)	81.731 (5), 86.437 (5), 71.422 (5)
V (Å ³)	2810.9 (3)
Z	6
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.74
Crystal size (mm)	0.76 × 0.33 × 0.27
Data collection	
Diffractometer	Oxford-Diffraction XCALIBUR
Absorption correction	Multi-scan <i>CrysAlis RED</i> (Oxford Diffraction, 2007) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{\text{min}}, T_{\text{max}}$	0.762, 0.834
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24992, 13842, 10817
R_{int}	0.026
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.105, 1.15
No. of reflections	13844
No. of parameters	733
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.02, -1.10

Computer programs: *CrysAlis CCD* (Oxford Diffraction, 2007), *CrysAlis RED* (Oxford Diffraction, 2007), *CrysAlis RED, SIR97* (Altomare *et al.*, 1999), *SHELXL97* (Sheldrick, 1997), *ORTEP-III* (Burnett & Johnson, 1996); *ORTEP-3 for Windows* (Farrugia, 1997); *CAMERON* (Pearce *et al.*, 2000); *PLATON* (Spek, 2003), *WinGX* publication routines (Farrugia, 1999).

Table 2

Hydrogen-bond geometry (Å, °) for (I)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O16—H1 \cdots O22	0.84	1.96	2.748 (4)	156
O26—H2 \cdots O32	0.84	1.90	2.719 (4)	164
O36—H3 \cdots O12 ⁱ	0.84	1.89	2.714 (4)	169
N12—H12 \cdots O15	0.88	1.92	2.599 (4)	133
N12—H12 \cdots O13	0.88	2.35	3.165 (4)	153
N22—H22 \cdots O25	0.88	1.90	2.577 (4)	132
N22—H22 \cdots O23	0.88	2.41	3.230 (4)	155
N32—H32 \cdots O35	0.88	1.94	2.609 (4)	132
N32—H32 \cdots O33	0.88	2.32	3.124 (4)	153

Symmetry code: (i) $x-1, y+1, z+1$.**Table 3**

Table 2 Structure matching between the three independent molecules and between the two polymorphs.

A is the structure matching between Molecules 1 and 2 in the Title structure

B is the structure matching between Molecules 1 and 3 in the Title structure

C is the structure matching between Molecules 2 and 3 in the Title structure

D is the structure matching between the two polymorphs

Overlay	RMS position (Å)	RMS bond (Å)	RMS torsion (°)
A	0.1459	0.0071	2.8944
B	0.1084	0.0085	3.7916
C	0.1702	0.0089	5.2911
D	0.182	0.783	9.806

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Figure 1

Fig. 1. The asymmetric unit of (**I**) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bondings have been omitted for clarity.

Figure 2

Fig. 2. Scheme showing the two enantiomers with the priority numbers used to define the absolute configuration shown as indices.

Figure 3

Fig. 3. Partial packing view of compound (**I**), showing the formation of chains along $[-1\ 1\ 1]$ built from hydrogen bonds. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

Figure 4

Fig. 4. Overlays of the different molecules within the Title compound **A**, **B** and **C** and an overlay of the two polymorphs **D**.

Figure 5

Fig. 5 View of the simulated powder patterns for both polymorph (**I**) and (**II**).

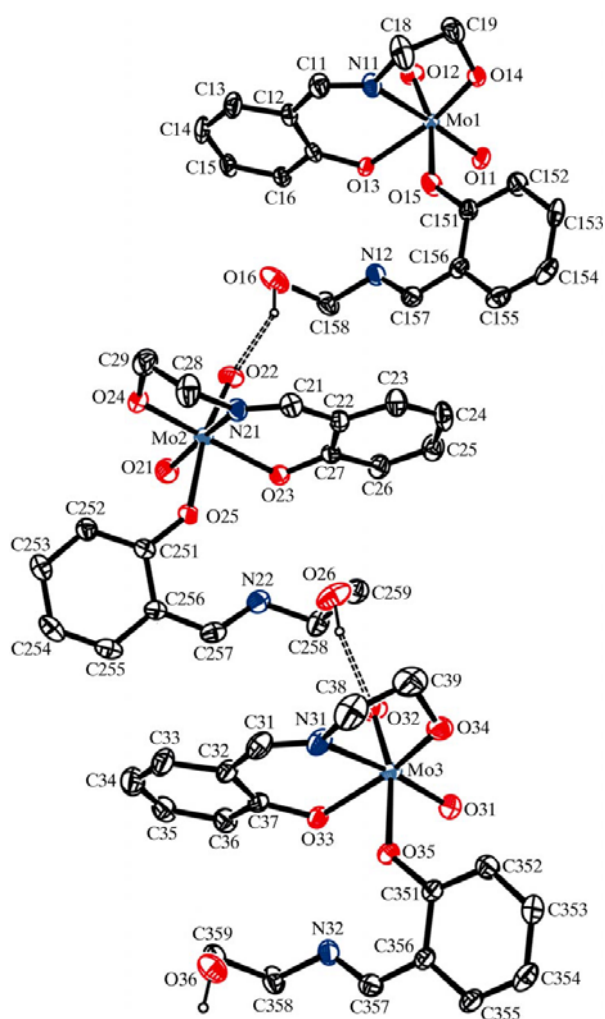
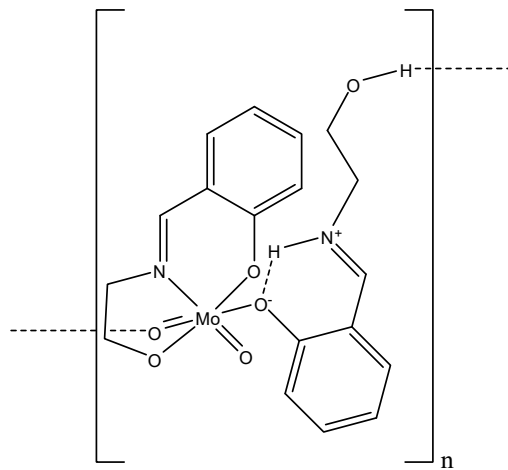


Fig. 1

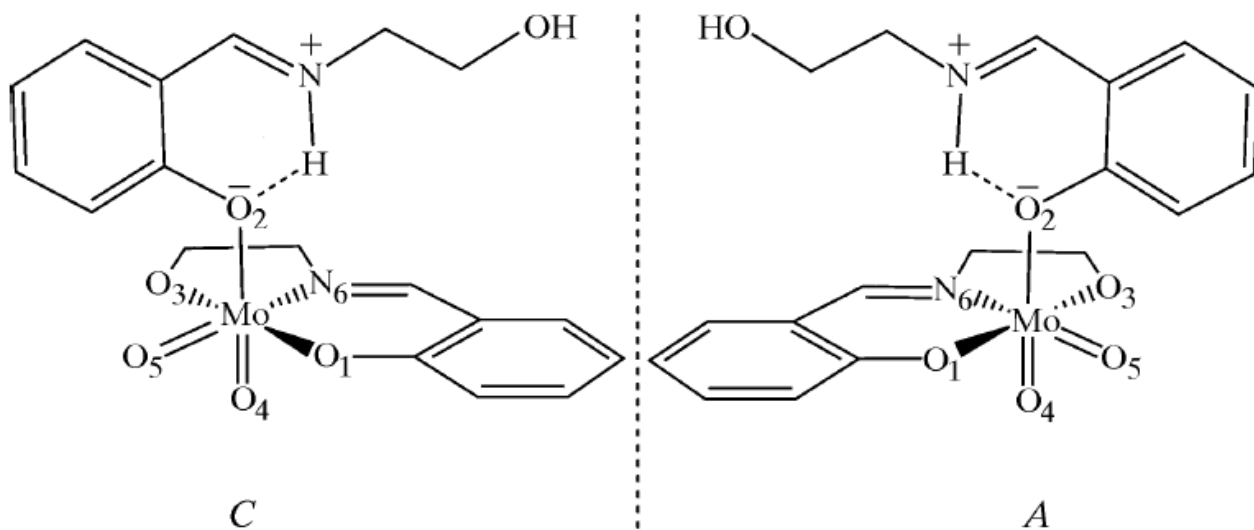


Fig. 2

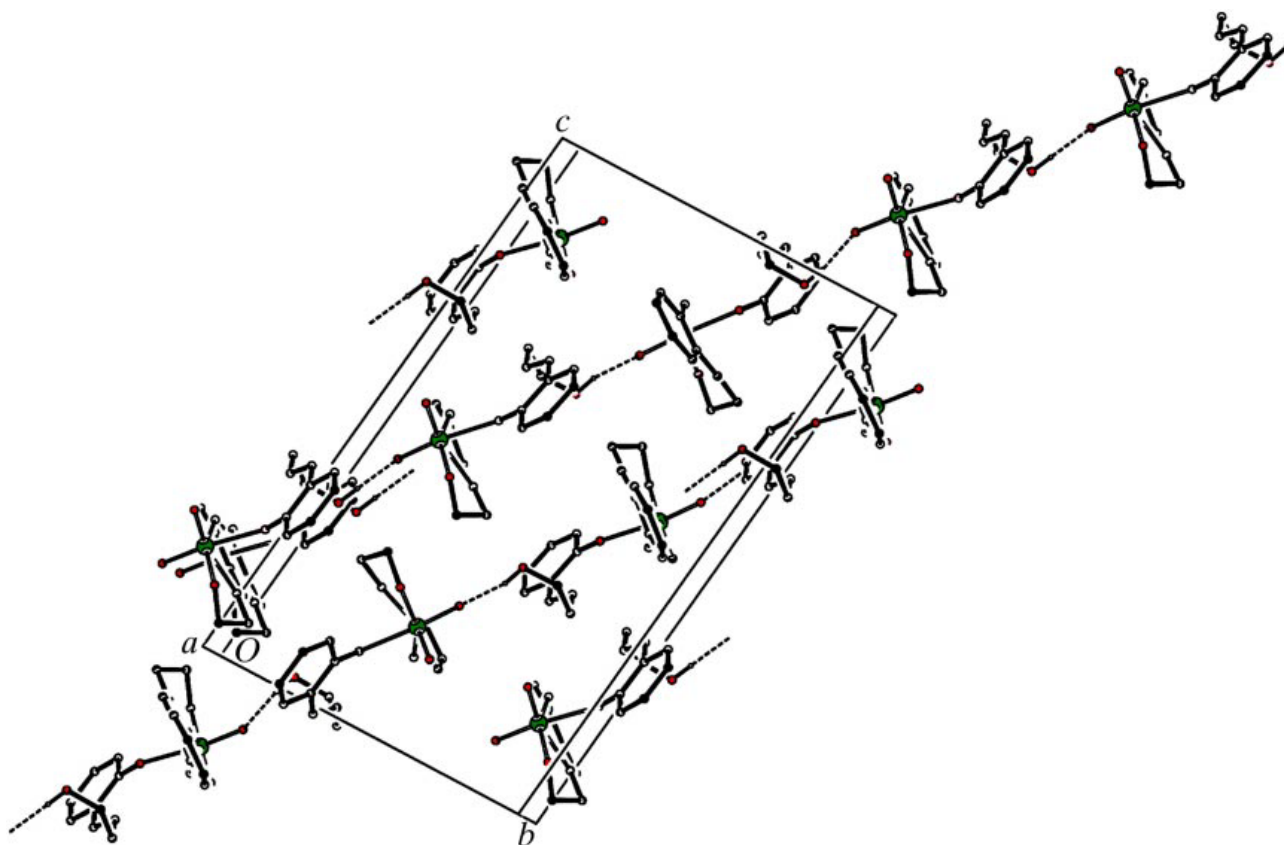


Fig. 3

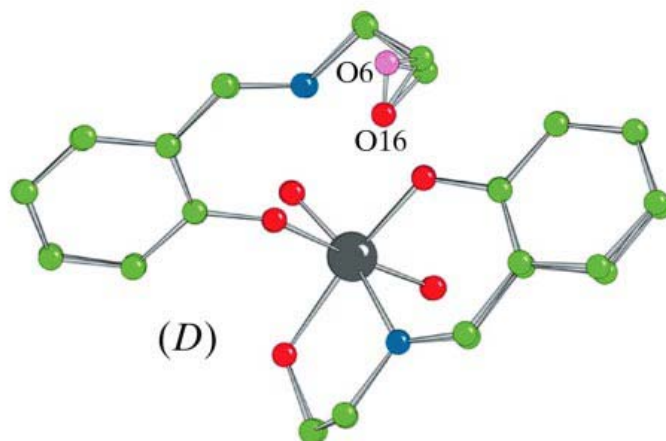
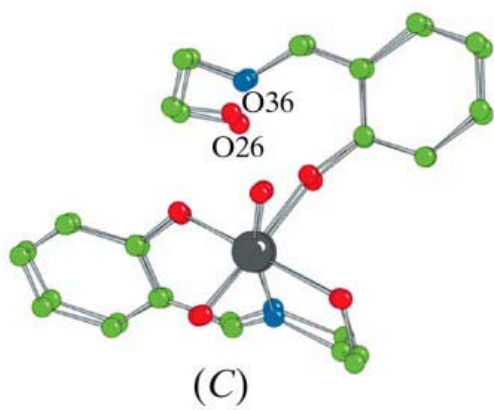
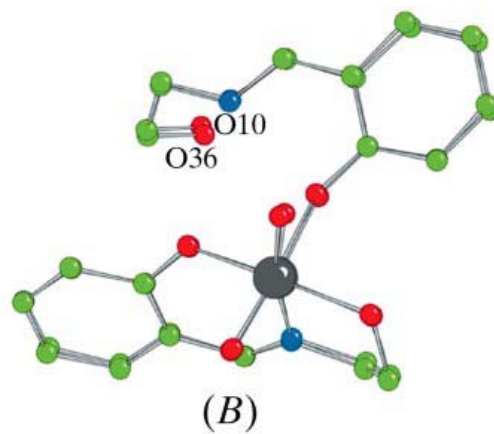
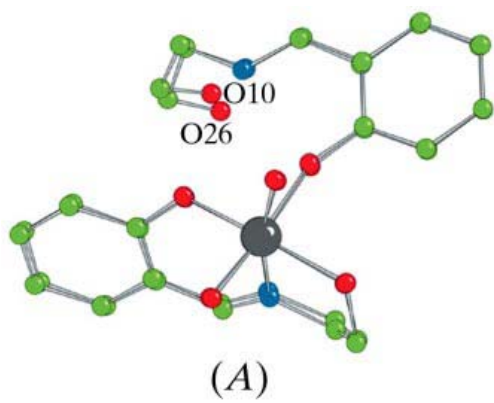


Fig. 4

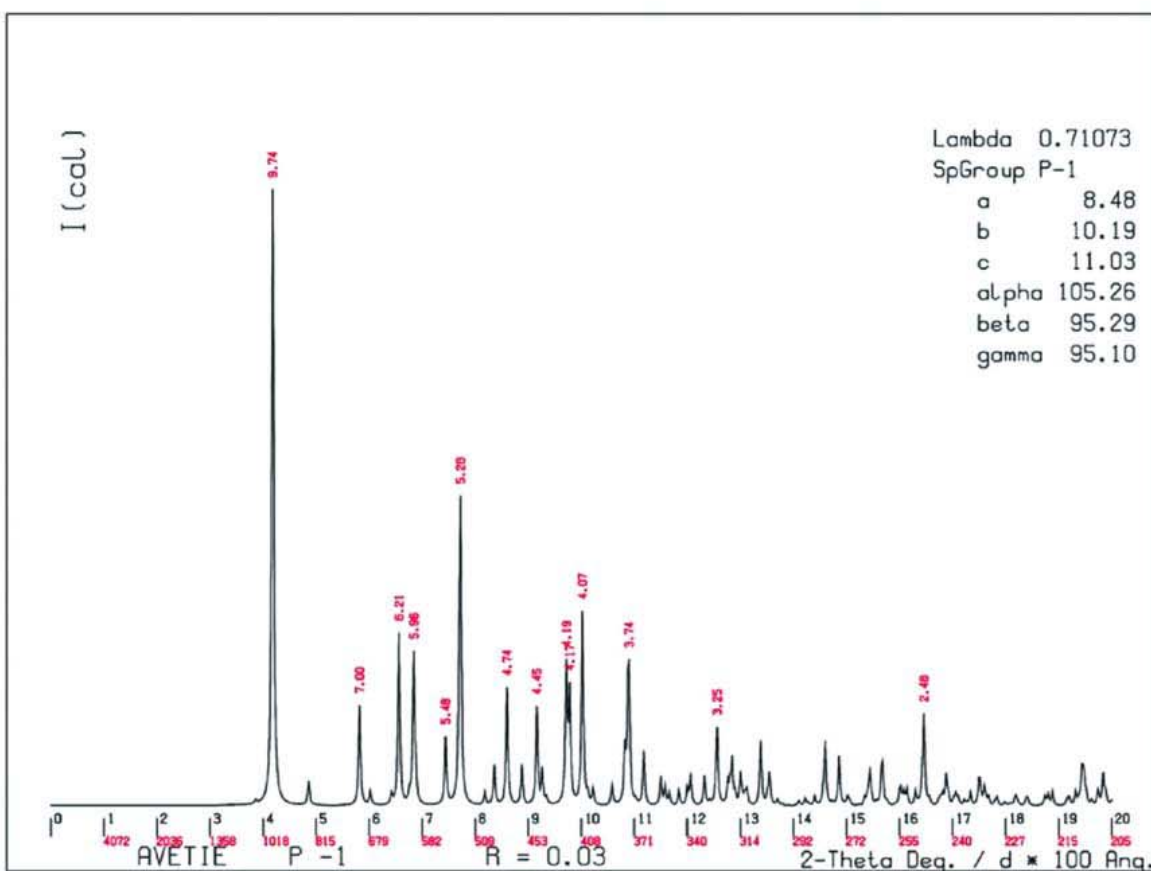
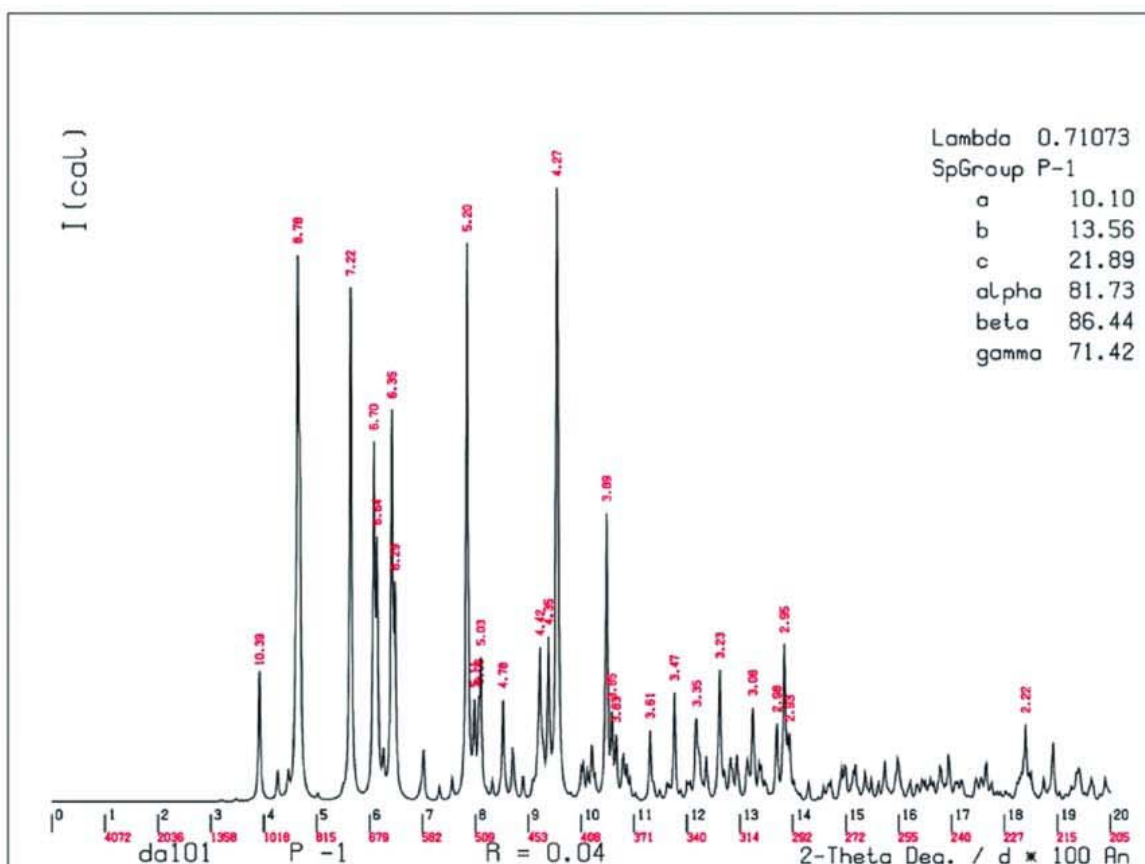


Fig. 5