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Polymorph of {2-[(2-hydroxyethyl)iminiomethyl]phenolato-*κO*}dioxido{2-[(2-oxidoethyl)iminomethyl]phenolato-κ^3*O*,*N*,*O*′}molybdenum(VI)

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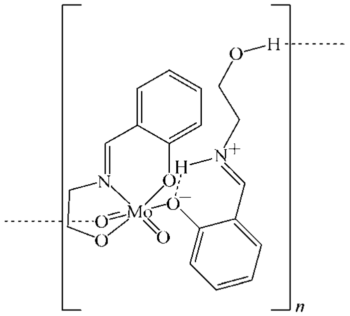
A second polymorphic form (form I) of the previously reported compound {2-[(2-hydroxyethyl)iminiomethyl]phenolato-*κO*}dioxido{2-[(2-oxidoethyl)iminomethyl]phenolato-κ^3*O*,*N*,*O*′}molybdenum(VI) (form II), $[Mo(C_9H_9NO_2)O_2(C_9H_{11}NO_2)]$, is presented. The title structure differs from the previously reported polymorph [Głowiak, Jerzykiewicz, Sobczak & Ziółkowski (2003). *Inorg. Chim. Acta*, **356**, 387–392] 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 $[\overline{1}11]$ direction. As in the previous polymorph, each molecule is built up from an MoO_2^{2+} cation surrounded by an *O*,*N*,*O*′-tridentate ligand ($O^-C_6H_4CH{=}NCH_2CH_2O^-$) and weakly coordinated by a second zwitterionic ligand ($O^-C_6H_4CH{=}N^+HC_2H_4OH$). All complexes are chiral with the absolute configuration at Mo being *C* or *A*. The main difference between the two polymorphs results from the alternation of the chirality at Mo within the chain.

Comment

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 are interested in investigating the catalytic activity of Mo^{VI} complexes linked to tridentate ligands, we have synthesized and structurally characterized the title compound, (I), and compare it with the previously published polymorph, (II) (Głowiak *et al.*, 2003).

Reaction of $MoO_2(sal)_2$ (sal is salicylate) with ethanolamine ($HOCH_2CH_2NH_2$) under the conditions described by Głowiak *et al.* (2003) led to a new polymorphic crystalline structure of $MoO_2(1,2\text{-}OC_6H_4CH{=}NC_2H_4O)(1,2\text{-}O^-C_6H_4CH{=}N^+HC_2H_4OH)$ with three crystallographically independent molecules per unit cell. The two polymorphs crystallize in the triclinic space group $P\overline{1}$ with different cell parameters [(I): a = 10.096 Å, b = 13.565 Å, c = 21.879 Å, α = 81.68°, β = 86.40°, γ = 71.41°, V = 2810.9 Å^3 and Z = 6; (II): a = 8.483 Å, b = 10.187 Å, c = 11.034 Å, α = 105.26°, β = 95.29°, γ = 95.10°, V = 909.6 Å^3 and Z = 2].



(I)

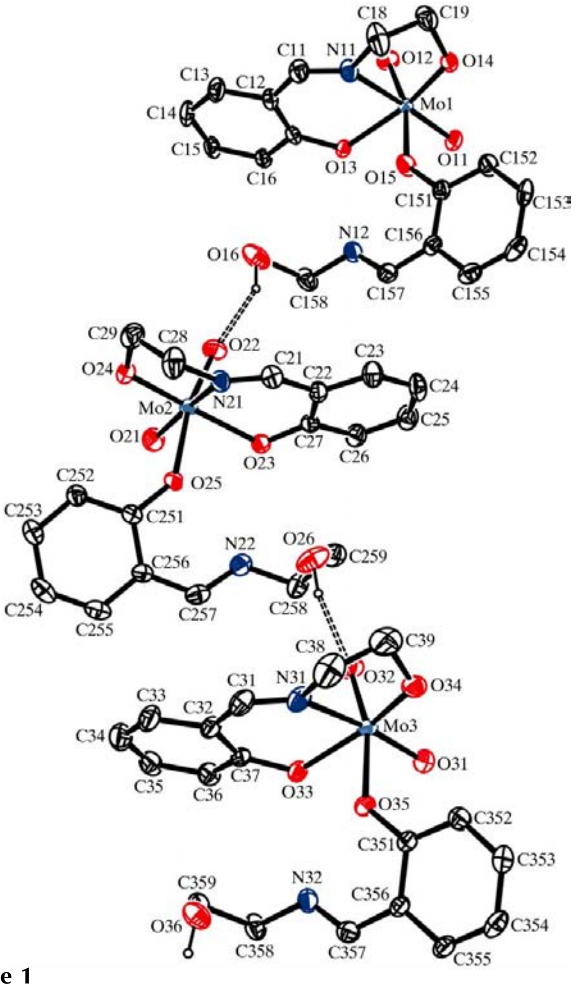


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonds have been omitted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

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For both (I) and (II), the molecule is based on an MoO_2^{2+} cation surrounded by a doubly charged anionic *O*,*N*,*O*′-tridentate ligand ($O^-C_6H_4CH{=}NCH_2CH_2O^-$) and weakly O-coordinated to a zwitterionic ligand ($O^-C_6H_4CH{=}N^+H$-C_2H_4OH) (Fig. 1). The zwitterionic form is stabilized by intramolecular N—H⋯O hydrogen bonds between the N^+H group and the O atom within the same ligand linked to the Mo atom. A second weak interaction may be noted between the same N^+H group and one of the O atoms of the tridentate ligand (O13, O23 or O33; Table 1).

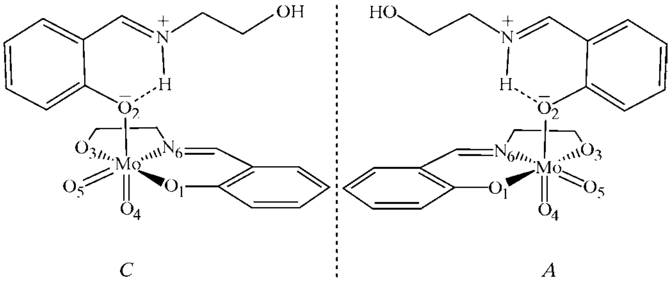

Figure 2
The two enantiomers, *C* and *A*, with the priority numbers used to define the absolute configuration shown as subscripted indices.

All the crystallographically independent complexes are chiral at Mo, and the absolute configuration of each Mo atom could be determined as either *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, (I), differs from structure (II) by the fact that the asymmetric unit of (I) contains three molecules linked by O—H⋯O hydrogen bonds (Table 1) involving the hydroxyl O atom of the zwitterionic ligand of one molecule to an oxo O atom attached to the Mo atom of another molecule. These trimeric units are further linked through O—H⋯O hydrogen bonds of the same type to form a chain parallel to the $[\overline{1}11]$ direction (Fig. 3).

Although the chirality is different for each molecule, they have roughly the same conformation. Indeed, an overlay

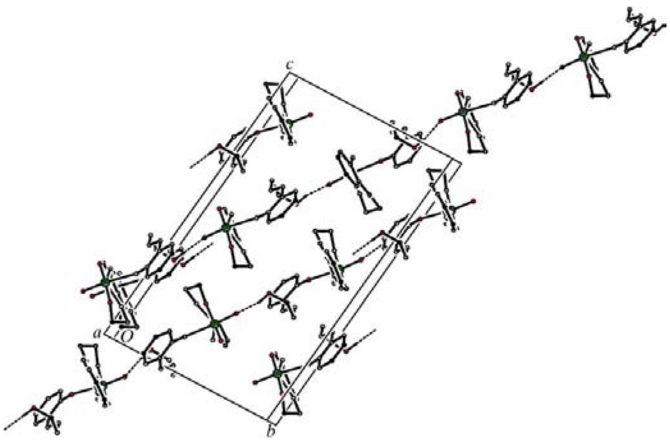

Figure 3
A partial packing view of compound (I), showing the formation of chains along $[\overline{1}11]$ built from hydrogen bonds. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

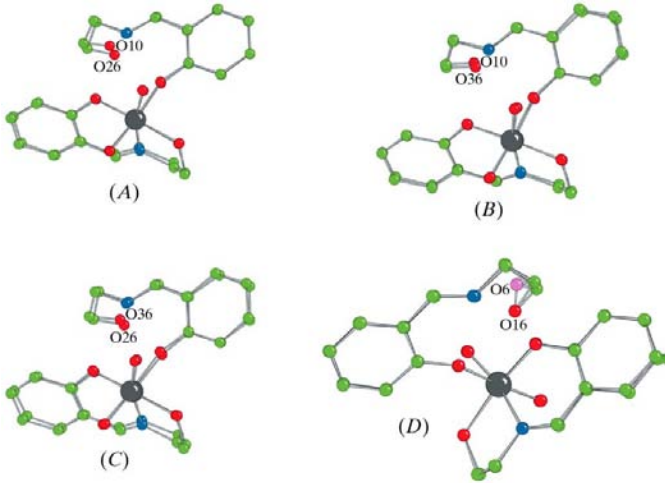

Figure 4
Overlays of the different molecules within the title compound, (*A*), (*B*) and (*C*), and an overlay of the two polymorphs, (*D*); see also Table 2.

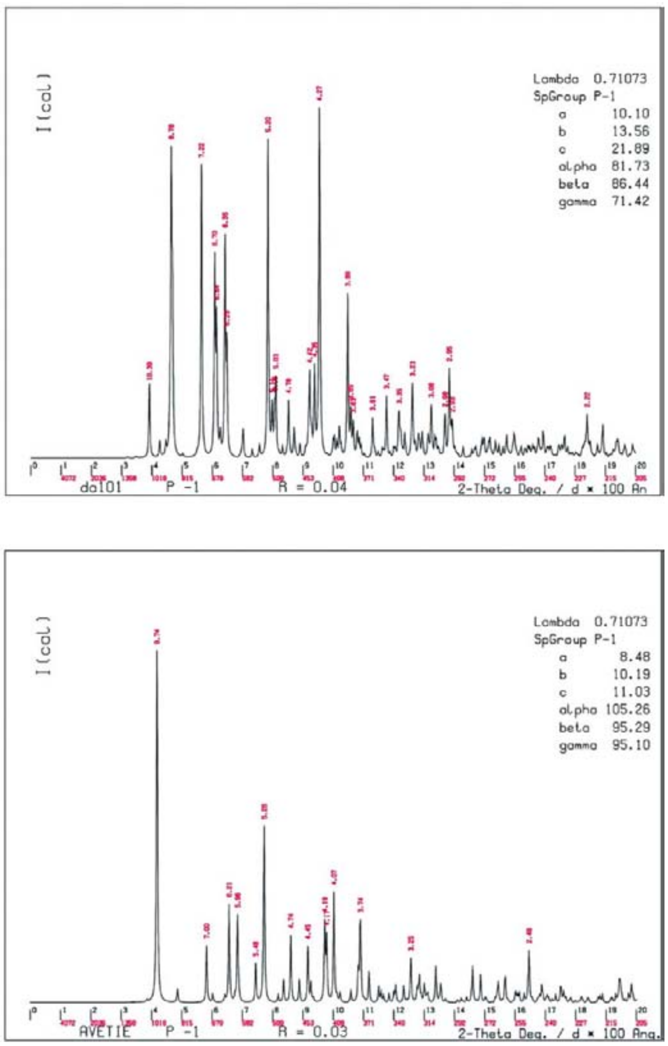

Figure 5
A view of the simulated powder patterns for polymorphs (I) (top) and (II) (bottom).

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analysis calculated using structure-matching software (Watkin *et al.*, 2003; Collins *et al.*, 2006) shows that the three molecules can be superimposed (Fig. 4 and Table 2). A similar overlay analysis of the two polymorphs indicates that the largest deviation occurs for the dangling hydroxyl O atom (Fig. 4) not coordinated to the Mo atom and involved in hydrogen bonding, which is not surprising owing to the different packing observed in the two isomers. However, it is worth pointing out that in compound (II), the chain is formed from complexes having the same configuration *C* (or *A*), whereas in compound (I), the chain is built up from trimeric units linked by translation to form infinite $(CAC)_n$ [or $(ACA)_n$] 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 $–CH_2NHCH_2CH_2OH$ chain over the chelating ligand is certainly induced by a second weak N—H···O interaction involving one of the O atoms (O13, O23 or O33) of the tridentate ligand (Table 1).

Experimental

More than two equivalents of $HOCH_2CH_2NH_2$ (0.3 ml, 4.97 mmol) were added to an ethanol solution (10 ml) of one equivalent of $MoO_2(sal)_2$ (0.92 g, 2.48 mmol), synthesized following a literature procedure (Yamanouchi & Yamada, 1974). The mixture was maintained under reflux for 30 min. The white precipitate that formed was separated off. The solution was subsequently cooled to room temperature and left to stand in air. Evaporation of the filtrate gave air-stable yellow crystals of the title compound, (I). The IR spectrum of the yellow crystals in KBr pellets showed no visible difference from that of the compound synthesized previously (Głowiak *et al.*, 2003).

Crystal data

$[Mo(C_9H_9NO_2)O_2(C_9H_{11}NO_2)]$
$M_r = 456.30$
Triclinic, $P\overline{1}$
$a = 10.0953\ (5)$ Å
$b = 13.5645\ (8)$ Å
$c = 21.8864\ (14)$ Å
$\alpha = 81.731\ (5)°$
$\beta = 86.437\ (5)°$
$\gamma = 71.422\ (5)°$
$V = 2810.9\ (3)$ Å^3
$Z = 6$
Mo $K\alpha$ radiation
$\mu = 0.74$ mm^{-1}
$T = 180\ (2)$ K
0.76 × 0.33 × 0.27 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2007); empirical (using intensity measurements) absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
$T_{min} = 0.762$, $T_{max} = 0.834$
24992 measured reflections
13842 independent reflections
10817 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 1.15$
13844 reflections
733 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -1.10$ e Å^{-3}

All H atoms were fixed geometrically and treated as riding, with C—H = 0.93 (aromatic) or 0.97 Å (methylene), O—H = 0.84 Å and N—H = 0.88 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$, $1.5U_{eq}(O)$ or $1.2U_{eq}(N)$. The two polymorphs have the same $P\overline{1}$ space group but no relation between them could be found. Moreover, the simulated powder patterns produced using *PLATON* (Spek, 2003) are different (Fig. 5).

Table 1
Hydrogen-bond geometry (Å, °).

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

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

Table 2
Structure matching between the three independent molecules of (I) and between the two polymorphs, (I) and (II).

(*A*) is the structure match between molecules 1 and 2 in the title structure, (*B*) is the structure match between molecules 1 and 3 in the title structure, (*C*) is the structure match between molecules 2 and 3 in the title structure, and (*D*) is the structure match between the two polymorphs.

Overlay	R.m.s. position (Å)	R.m.s. bond (Å)	R.m.s. 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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997), *CAMERON* (Pearce *et al.*, 2000) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3193). Services for accessing these data are described at the back of the journal.

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