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exo-[(*RS*,*SR*)-*N*,*N*′-Bis(salicylidene)-2,3-butanediaminato]oxovanadium(IV)

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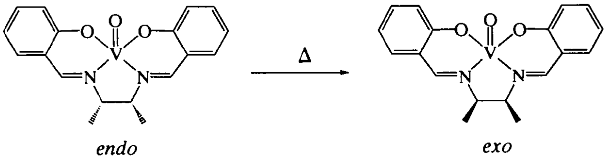
Abstract

The thermally more stable isomer of the title complex, {2,2′-[(*RS*,*SR*)-2,3-butanediylbis(nitrilomethylidene)]diphenolato-*O*,*N*,*N*′,*O*′}oxovanadium(IV), [$VO(C_{18}H_{18}N_2O_2)$] or [VO(sal-*meso*-bn)] [H_2sal-*meso*-bn is (*RS*,*SR*)-*N*,*N*′-bis(salicylidene)-2,3-butanediamine], in the solid state, has been determined to be the *exo* isomer. The two methyl groups of the central diamine moiety in the Schiff base ligand are on the same side of the N_2O_{oxo} plane of the VN_2O_3 square pyramid as the oxo ligand. The V=O distance is 1.595 (2) Å, and the V atom is displaced by 0.50 (1) Å toward the oxo ligand from the N_2O_2 basal plane. There is an intermolecular $V\cdots O_{salicyl}$ close contact of 2.972 (2) Å, which is *trans* to the V=O bond.

Comment

Certain oxovanadium(IV) complexes with Schiff base ligands show thermal isomerization and/or dehydrogenation of the Schiff base ligand in the solid state (Kojima *et al.*, 1994; Hoshina *et al.*, 1998). The title complex shows thermal isomerization at 483 K. For this complex, there are two possible geometrical isomers, *endo* and *exo*, arising from the disposition of the substituents of the alkyldiamine moiety of the Schiff base ligand relative to the VN_2O_3 square pyramid. In this paper, the structure of the more stable *exo* isomer, (I), is reported.



(I)

As shown in Fig. 1, the two methyl groups at C14 and C16 are located on the same side as the oxo ligand, O2. This is the *exo* isomer. The present study reveals that thermal isomerization of the title complex occurs in the solid state from the *endo* to the *exo* isomer. The central five-membered chelate ring adopts a symmetric skew conformation. The methyl groups on C14 and C16 are in axial and equatorial positions, respectively, to the five-membered chelate ring.

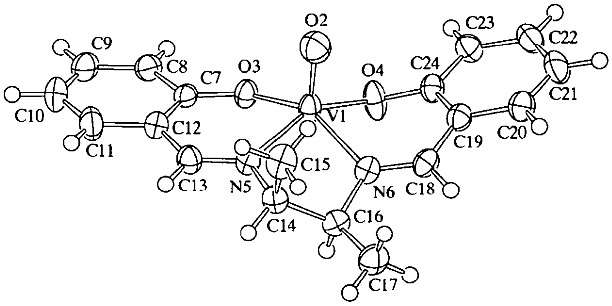


Fig. 1. The molecular structure of (I) showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The crystal structure of (I) is shown in Fig. 2. The complexes form a weak dimeric structure around the centre of symmetry through cyclic $V1\cdots O4^{i}$—$V1^{i}\cdots O4$ interactions, with a $V1\cdots O4^{i}$ distance of 2.972 (2) Å [symmetry code: (i) $1-x$, $-y$, $2-z$]. This interaction causes the deformation of the six-membered chelate ring in which atom O4 is included. The V1—O4—C24—C19 torsion angle is 41.3 (3)°, in contrast with the V1—O3—C7—C12 angle of −17.8 (3)°. The sharing of the $O_{salicyl}$ atom by two V atoms has been observed in a tetramer, $[\{V(salen)\}_2O_2](I_3)_2 \cdot CH_3CN$ (Hughes *et al.*, 1994), where H_2salen is *N*,*N*′-bis(salicylidene)ethylenediamine. The dimeric structures of salen complexes with strong cyclic $M—O_{salicyl}—M—O_{salicyl}$ bonds have been reported for several metal atoms: $[Mn(salen)(H_2O)]_2(ClO_4)_2 \cdot 2H_2O$ (Garcia-Deibe *et al.*, 1991), $[Fe(salen)Cl]_2$ (Gerloch & Mabbs, 1967), $[Fe(salen)NO_3]_2$ (Resce *et al.*, 1987), $[Co(salen)]_2$ (Bruckner *et al.*, 1969), $[Co(salen)Cl]_2 \cdot CHCl_3$ (Eichhorn *et al.*, 1993) and $[Cu(salen)]_2$ (Bhadbhade & Srinivas, 1993).

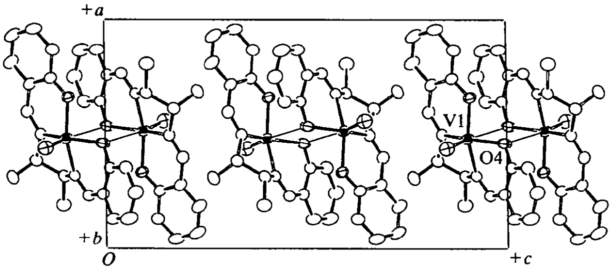


Fig. 2. Projection of the crystal structure of (I) along **b**. Intermolecular $V \cdots O_{salicyl}$ close contacts are indicated by thin solid lines.

Experimental

To a solution of H_2sal-*meso*-bn (0.30 g, 1 mmol) in dichloromethane (10 ml) was added a solution of $[VO(acac)_2]$ (0.27 g, 1 mmol) in dichloromethane (10 ml) (H_2acac is 2,4-pentanedione). The mixture was stirred for 1 h and evaporated to dryness. The resulting green powder was collected and washed with ether; yield of [VO(sal-*meso*-bn)] = 0.33 g (91%). Analysis calculated for $C_{18}H_{18}N_2O_3V$: C 59.84, H 5.02, N 7.75%; found: C 59.71, H 4.88, N 7.82%. The product was a mixture of *endo* and *exo* isomers (*endo*:*exo* ≃ 1:1); the ratio of isomers was estimated by high-performance liquid chromatography. The powder containing this mixture of isomers was kept at 483 K for 50 h under an argon atmosphere to convert it into a single isomer, (I). Crystals of (I) were obtained from an acetonitrile solution by slow evaporation.

Crystal data

$[VO(C_{18}H_{18}N_2O_2)]$
$M_r = 361.29$
Monoclinic
$P2_1/c$
$a = 10.796 (3)$ Å
$b = 7.755 (2)$ Å
$c = 19.315 (2)$ Å
$\beta = 90.80 (1)°$
$V = 1616.9 (5)$ Å^3
$Z = 4$
$D_x = 1.484$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.7–15.0°$
$\mu = 0.632$ mm^{-1}
$T = 297$ K
Sphere
0.25 mm (radius)
Green

Data collection

Rigaku AFC-5 diffractometer
$\theta/2\theta$ scans
Absorption correction: spherical (*International Tables for Crystallography*, 1992, Vol. C)
$T_{min} = 0.787$, $T_{max} = 0.791$
3896 measured reflections
3702 independent reflections

2932 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -25 \rightarrow 25$
3 standard reflections every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.036$
$wR = 0.064$
$S = 1.262$
3702 reflections
235 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o) + 0.00123|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

V1—O2	1.595 (2)	V1—N5	2.061 (2)
V1—O3	1.937 (2)	V1—N6	2.068 (2)
V1—O4	1.948 (2)		
O3—V1—N5	88.05 (7)	N5—V1—N6	78.53 (7)
O4—V1—N6	86.20 (7)		
V1—O3—C7—C12	−17.8 (3)	V1—N6—C16—C14	−36.9 (2)
V1—O4—C24—C19	41.3 (3)	V1—N6—C16—C17	−165.3 (2)
V1—N5—C14—C15	84.8 (2)	N5—C14—C16—N6	46.0 (2)
V1—N5—C14—C16	−38.0 (2)		

The refinements were carried out based on all independent reflections. The threshold, $I > 2\sigma(I)$, was only used for calculation of the R factor. All H-atom positions were calculated geometrically, and only their displacement parameters were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1084). Services for accessing these data are described at the back of the journal.

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Di-μ-aqua-bis[(trimethanol-*O*)sodium] *anti*-bis(μ-2-propanethiolato-*S*:*S*)bis[bis(2-propanethiolato-*S*)iron(II)] and bis(benzyltrimethylammonium) *anti*-bis(μ-2-propaneselenolato-*Se*:*Se*)bis[bis(2-propaneselenolato-*Se*)iron(II)]

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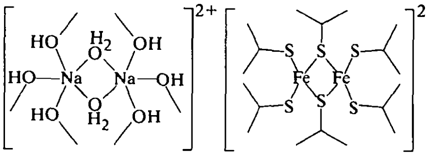
Abstract

In the $[Fe_2(S^iC_3H_7)_6]^{2-}$ and $[Fe_2(Se^iC_3H_7)_6]^{2-}$ complex anions of the title compounds, $[Na_2(CH_4O)_6(H_2O)_2][Fe_2(C_3H_7S)_6]$ and $(C_{10}H_{16}N)_2[Fe_2(C_3H_7Se)_6]$, the Fe atoms are coordinated by four chalcogen atoms in a distorted tetrahedral fashion. The FeE_4 tetrahedra of the Fe_2E_6 frameworks (E = S or Se) share a common edge. The central Fe_2E_2 unit is an exactly planar rhomb with acute M—E—M angles. The oxidation state of iron is +2. The $[Fe_2(S^iC_3H_7)_6]^{2-}$ anion was crystallized with the novel counter-cation $[(MeOH)_3Na(H_2O)_2Na(MeOH)_3]^{2+}$.

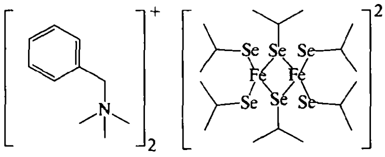
Comment

Iron–chalcogenolate and mixed iron–chalcogenide–chalcogenolate complexes have been studied extensively due to their importance as model compounds for enzyme centres (Holm *et al.*, 1990; Krebs & Henkel, 1991). The homoleptic iron(II)–chalcogenolate complexes with sterically unencumbered monofunctional chalcogenolate ligands contain iron in a tetrahedral chalcogen environment. Within this class of complexes, mononuclear (Millar *et al.*, 1982, 1984), dinuclear (Hagen & Holm, 1984) and tetranuclear species (Hagen *et al.*, 1982) are known. Recently, a novel type of a dinuclear iron–thiolate complex was described (Henkel & Chen, 1993). This complex consists of two approximately tetrahedral $[Fe(SR)_4]$ units which share a common face. The nucleophilicity of the ligands are expected to be of importance for stabilizing this unusual degree of condensation. Transition metal complexes with bitetrahedral M_2S_5 units have been described with secondary (Henkel & Weißgräber, 1992) and tertiary alkane chalcogenolate ligands (Weißgräber, 1994; Henkel & Weißgräber, 1999). Related complexes containing substituted thiophenolate groups are also known (Ruhlandt-Senge & Power, 1993; Silver & Millar, 1992).

During our investigations of the reaction behaviour of iron(II) towards secondary alkane chalcogenolate ligands, we were able to isolate the compounds $[(MeOH)_3Na(H_2O)_2Na(MeOH)_3][Fe_2(S^iC_3H_7)_6]$, (1), and $[BzMe_3N]_2[Fe_2(Se^iC_3H_7)_6]$, (2). Compound (1) is the product of the reaction of iron(II) chloride with sodium 2-propanethiolate in methanol, whereas (2) was obtained by reaction of iron(II) chloride with sodium 2-propaneselenolate and benzyltrimethylammonium bromide in acetonitrile.



(1)



(2)

Crystals of (1) and (2) consist of discrete $[Fe_2(E^iC_3H_7)_6]^{2-}$ (E = S or Se) complex anions and isolated counter-cations, namely $[(MeOH)_3Na(H_2O)_2Na(MeOH)_3]^{2+}$ in the case of (1) and $[BzMe_3N]^+$ in the case of (2). The $[Fe_2(S^iC_3H_7)_6]^{2-}$ and $[Fe_2(Se^iC_3H_7)_6]^{2-}$ anions have crystallographically imposed

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