

Hydrogen-bonded sheets in racemic *cis*-(2,2'-bipyridyl- κ^2N,N')oxo-(pentane-2,4-dionato- κ^2O,O')-(thiocyanato- κN)vanadium(IV)

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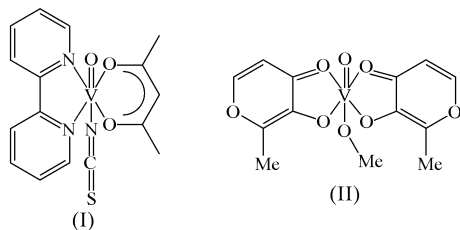
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The title compound, $[V(C_5H_7O_2)(NCS)O(C_{10}H_8N_2)]$, crystallizes with $Z' = 2$ in the space group *Pbca*. The molecules are linked into sheets by a combination of four C—H···O hydrogen bonds and one C—H···N hydrogen bond. The four C—H···O hydrogen bonds generate chains of rings, where each chain contains just a single enantiomer of each of the two independent molecules, while the C—H···N hydrogen bond generates a chain containing both enantiomers of just one of the independent molecules.

Comment

The reactions of tris(pentane-2,4-dionato)vanadium(III) with salts of 2,2'-bipyridine and 1,10-phenanthroline containing non-coordinating anions have been used to prepare six-coordinate mixed-ligand complexes of vanadium (Kavitha *et al.*, 2006, 2006*a*). In an attempt to prepare seven-coordinate V^{III} complexes using salts containing coordinating anions, the reaction of tris(pentane-2,4-dionato)vanadium(III) with 2,2'-bipyridinium thiocyanate was carried out. This resulted in the formation of the title compound, (I), an oxidized six-coordinate mixed-ligand complex of vanadium(IV).



Compound (I) (Fig. 1) crystallizes with $Z' = 2$ in the space group *Pbca*. The oxo and thiocyanate ligands occupy mutually *cis* sites in both of the independent molecules, so that these

molecules are chiral although the compound is racemic. The centrosymmetric space group accommodates equal numbers of Λ and Δ enantiomers, and in the selected asymmetric unit both molecules have the Λ configuration.

Because of the chemical hardness of the vanadium(IV) centre, the thiocyanate ligand coordinates *via* the N atom rather than *via* the S atom. The interbond angles at vanadium indicate some distortion from the ideal octahedral geometry and this may be dominated by the rather small bite angles (Table 1) characteristic of the bipyridyl ligands. The key bond distances and angles within the two independent molecules are very similar; in particular, both molecules contain VNCS fragments which are nearly linear.

Molecules of (I) are linked into complex sheets by a combination of four C—H···O hydrogen bonds and one C—H···N hydrogen bond (Table 2). The sheet formation is readily analysed in terms of two one-dimensional substructures, one involving all of the C—H···O hydrogen bonds and the other depending on just the single C—H···N hydrogen

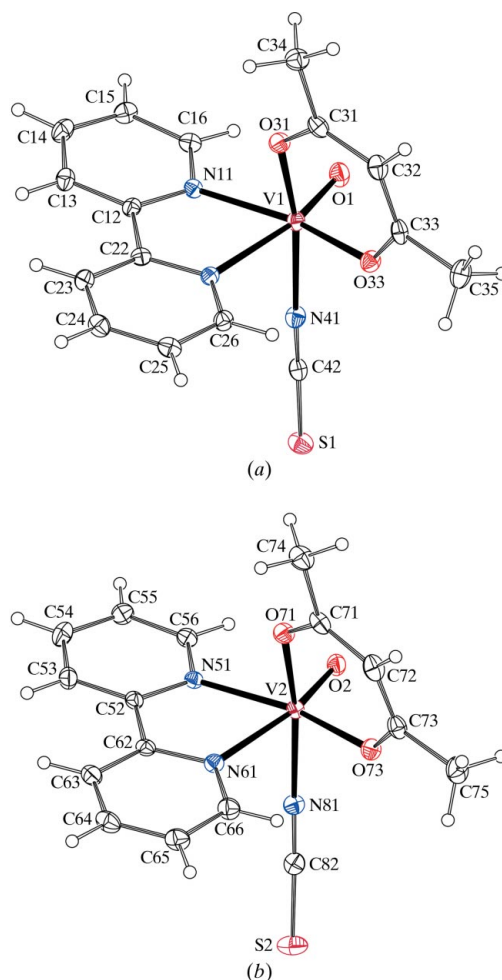


Figure 1

The two independent Λ enantiomers of (a) the type 1 molecule and (b) the type 2 molecule in the selected asymmetric unit of compound (I), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 30% probability level.

bond. Within the selected asymmetric unit, atoms C53 and C63 flanking the bay region of the bipyridyl ligand in the type 2 molecule (containing atom V2) both act as hydrogen-bond donors to atom O1 in the type 1 molecule (containing atom

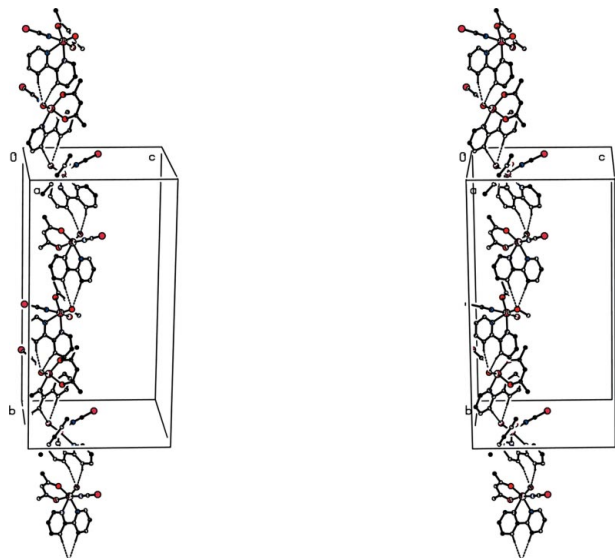


Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of rings along $(\frac{1}{2}, y, \frac{1}{4})$ containing Λ enantiomers only. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

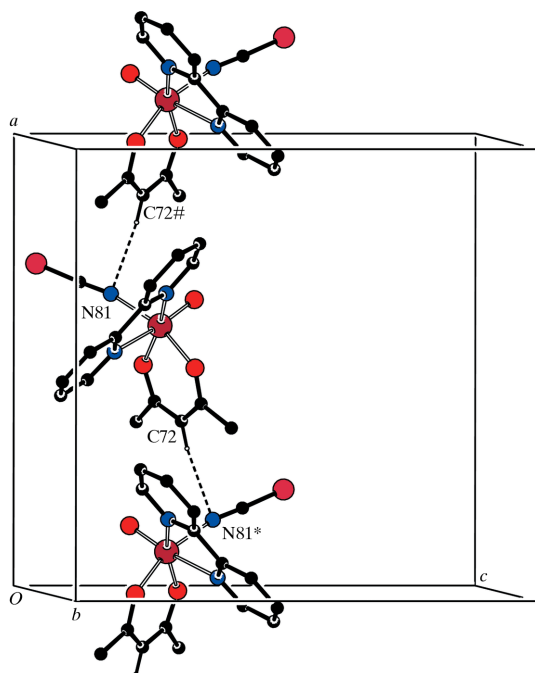


Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $C(6)$ chain along $[100]$. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$ and $(\frac{1}{2} + x, y, \frac{1}{2} - z)$, respectively.

V1). In addition, atoms C13 and C23 flanking the bay region of the bipyridyl ligand in the type 1 molecule at (x, y, z) both act as hydrogen-bond donors to atom O2 in the type 2 molecule at $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, so forming a complex chain of alternating chelate and hydrogen-bonded rings running parallel to the $[010]$ direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$ (Fig. 2). Four chains of this type, each of which includes both type 1 and type 2 molecules, run through each unit cell. The chains generated by the screw axes along $(0, y, \frac{1}{4})$ and $(\frac{1}{2}, y, \frac{1}{4})$ include only the Λ enantiomers, while those along $(0, y, \frac{3}{4})$ and $(\frac{1}{2}, y, \frac{3}{4})$ include only the Δ enantiomers. We may note here the contrast between the hydrogen-bonding behaviour of compound (I), where each of the independent oxo ligands acts as a double acceptor of $C-H \cdots O$ hydrogen bonds, and that of the analogous compound (II) (see scheme), where the oxo ligand plays no part in the hydrogen bonding (Kavitha *et al.*, 2006b).

The second substructure includes only the type 2 molecules, but both enantiomers of this molecule are present in each chain. Atom C72 of the pentanedionate ligand in the type 2 molecule at (x, y, z) acts as hydrogen-bond donor to thiocyanate atom N81 in the type 2 molecule at $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$, so forming a simple $C(6)$ (Bernstein *et al.*, 1995) chain of alternating Λ and Δ enantiomers running parallel to the $[100]$ direction and generated by the a -glide plane at $z = \frac{1}{4}$ (Fig. 3).

The combination of these $[100]$ and $[010]$ chains generates a complex (001) sheet. Two such sheets, related to one another by inversion and lying in the domains $0 < z < \frac{1}{2}$ and $\frac{1}{2} < z < 1$ pass through each unit cell, but there are no direction-specific interactions between adjacent sheets. In particular, $C-H \cdots \pi$ (arene) hydrogen bonds and π - π stacking interactions are both absent from the structure of (I).

Experimental

A mixture containing equimolar quantities of 2,2'-bipyridinium thiocyanate and tris(pentane-2,4-dionato)vanadium(III) in methanol was heated under reflux for 3 h in a dinitrogen atmosphere. The mixture was cooled to ambient temperature and the solvent was removed under reduced pressure to yield crystals of (I) (m.p. 401 K) suitable for single-crystal X-ray diffraction analysis.

Crystal data

$[V(C_5H_7O_2)(NCS)O(C_{10}H_8N_2)]$
 $M_r = 380.32$
 Orthorhombic, $Pbca$
 $a = 15.0522$ (10) Å
 $b = 29.721$ (2) Å
 $c = 15.3753$ (10) Å
 $V = 6878.4$ (8) Å³
 $Z = 16$
 $D_x = 1.469$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 7898 reflections
 $\theta = 3.0$ – 27.6°
 $\mu = 0.72$ mm⁻¹
 $T = 120$ (2) K
 Plate, brown
 $0.18 \times 0.10 \times 0.04$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{min} = 0.882$, $T_{max} = 0.972$
 40301 measured reflections

7898 independent reflections
 5904 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.064$
 $\theta_{max} = 27.6^\circ$
 $h = -19 \rightarrow 19$
 $k = -32 \rightarrow 38$
 $l = -19 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.135$
 $S = 1.13$
 7898 reflections
 437 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 3.5919P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.77 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

V1—O1	1.603 (2)	V2—O2	1.608 (2)
V1—O31	2.000 (2)	V2—O71	1.998 (2)
V1—O33	1.967 (2)	V2—O73	1.963 (2)
V1—N11	2.133 (2)	V2—N51	2.142 (2)
V1—N21	2.270 (2)	V2—N61	2.261 (2)
V1—N41	2.044 (3)	V2—N81	2.032 (3)
N41—C42	1.164 (4)	N81—C82	1.161 (4)
C42—S1	1.633 (3)	C82—S2	1.626 (3)
N11—V1—N21	72.92 (8)	N51—V2—N61	73.02 (9)
V1—N41—C42	175.5 (2)	V2—N81—C82	168.1 (2)
N41—C42—S1	179.4 (3)	N81—C82—S2	177.1 (3)

Table 2
 Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13 \cdots O2 ⁱ	0.95	2.55	3.500 (4)	179
C23—H23 \cdots O2 ⁱ	0.95	2.52	3.468 (4)	177
C53—H53 \cdots O1	0.95	2.40	3.323 (4)	163
C63—H63 \cdots O1	0.95	2.52	3.441 (4)	165
C72—H72 \cdots N81 ⁱⁱ	0.95	2.53	3.457 (4)	166

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, y, -z + \frac{1}{2}$.

The space group $Pbca$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (ring H)

or 0.98 \AA (methyl H), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl groups.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3005). Services for accessing these data are described at the back of the journal.

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