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A new vanadate containing helical chains

Guo-Ming Wang,[a]* Jin-Hua Li,[b] Jing Han[a] and Hui-Luan Liu[a]

[a]Department of Chemistry, Teachers College of Qingdao University, Qingdao, Shandong 266071, People's Republic of China, and [b]Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
Correspondence e-mail: gmwang_pub@163.com

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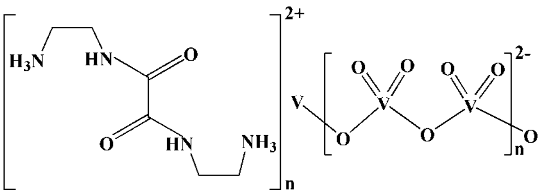
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.029; wR factor = 0.078; data-to-parameter ratio = 14.3.

The structure of a new vanadium oxide compound, *catena*-poly[N,N'-bis(2-ammonioethyl)oxamide [dioxidovanadate-μ-oxido-dioxidovanadate-μ-oxido]], $\{(C_6H_{16}N_4O_2)[V_2O_6]\}_n$, exhibits helical vanadate chains, constructed from corner-sharing VO_4 tetrahedra. Adjacent chains are packed together by extensive hydrogen bonds involving the inorganic framework and the templating guest cations, which are centrosymmetric and occupy the free space between the stacks of chains.

Related literature

For related literature, see: Cheetham *et al.* (1999); Chirayil *et al.* (1998); Hagrman & Zubieta (2000); Hagrman *et al.* (2001); Khan *et al.* (2000); Liu *et al.* (2002); Nazar *et al.* (1996); Ojima & Nonoyama (1988); Zhang *et al.* (1996).



Experimental

Crystal data

$(C_6H_{16}N_4O_2)[V_2O_6]$
M_r = 374.11
Monoclinic, $P2_1/n$
a = 6.7453 (3) Å
b = 5.5087 (1) Å
c = 18.1775 (2) Å
β = 100.114 (3)°
V = 664.94 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.45 mm^{-1}
T = 295 (2) K
0.20 × 0.12 × 0.08 mm

Data collection

Siemems SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.760, T_{max} = 0.893
4832 measured reflections
1300 independent reflections
1217 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.078
S = 1.11
1300 reflections
91 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected bond lengths (Å).

V—O1	1.6197 (18)	V—O3^{i}	1.8063 (17)
V—O2	1.6322 (19)	V—O3	1.8127 (17)

Symmetry code: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{ii}	0.86	2.24	3.013 (3)	149
N2—H2C···O3^{iii}	0.89	2.01	2.799 (3)	148
N2—H2E···O4^{iv}	0.89	1.96	2.833 (3)	167
N2—H2D···O2	0.89	1.96	2.705 (3)	140

Symmetry codes: (ii) $x, y+1, z$; (iii) $x-1, y, z$; (iv) $-x, -y+2, -z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2076).

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supplementary materials

Acta Cryst. (2007). E**63**, m2189 [**doi:10.1107/S160053680703471X**]

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G.-M. Wang, J.-H. Li, J. Han and **H.-L. Liu**

Comment

Microporous inorganic solids have attracted considerable attention in the past decades due to their structural diversity and potential applications in diverse areas (Cheetham *et al.*, 1999; Hagrman *et al.*, 2001). Among those, vanadium oxide family has proved a particularly rich source of new compounds. This is in part due to the flexible ability of vanadium to adopt tetrahedral, square-pyramidal, trigonal bipyramidal and octahedral coordination geometries, as well as their various oxidation states (III, IV and V). Besides, the utilizaion of hydrothermal technique in combination with cationic organic templates has also resulted in a huge number of new structures (Nazar *et al.*, 1996; Zhang *et al.*, 1996; Chirayil *et al.*, 1998; Hagrman & Zubieta, 2000; Khan *et al.*, 2000; Liu *et al.*, 2002). One may expect that the rational design of crystalline solids with complex architectures may be realised through shrewd choice of organic species. The aim of our work is to explore the construction of such materials, and a new chain-like vanadate (I), has been described here.

As shown in Fig. 1, the asymmetric unit contains only one half of a $[(H_2oxen)^{2+}$ ion. The V^V atom possesses a distorted tetrahedal geometry and is coordinated by two symetry related images of a bridging oxo group (O3) and two terminal unshared oxygen atoms (O1 and O2) with short vanadyl V=O bond distances (Table 1). The VO_4 tetrahedra are linked together through common vertices, leading to the formation of unusual helical –O—V—O—V—O– chains (Fig. 2). Adjacent chains are further stacked in an ABAB sequence along the *c* axis. The diprotonated templates H_2oxen, adopting the *transoid* conformation with an inversion centre at the mid-point of the $C1—C1^i$ bond [symmetry code: (i) $1 - x, 2 - y, -z$], fill the space of neighboring chains to compensate the negative charges and further extend the structure into 3-D supramolecular framework through hydrogen bonds with N···O distances in the range 2.705 (3)–3.013 (3) Å (Fig. 3).

Experimental

The Cu(oxen) was prepared according to the method of Ojima & Nonoyama (1988). A mixture of NH_4VO_3 (0.117 g,1.0 mmol), Cu(oxen) (0.118 g,0.5 mmol), $H_2C_2O_4·2H_2O$ (0.0257 g,0.2 mmol) and methanol (8 ml), was sealed in a 25 ml Teflon-lined steel autoclave and heated under autogenous pressure at 353 K for 6 h. Then, the filtrate was kept at room temperature and brown block-like crystals were obtained after a week.

Refinement

All the H atoms were positioned geometrically, with C—H = 0.97 Å and with N—H = 0.86 (NH) or 0.89 (NH_3) Å, and allowed to ride during refinement with $U_{iso}(H) = 1.2U_{eq}(C,N)$ for the CH_2 and NH groups or $1.5U_{eq}(N)$ for the NH_3 groups.

Figures

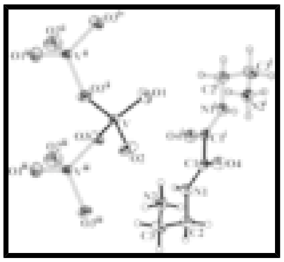


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids. [symmetry codes: (i) $1 - x$, $2 - y$, $-z$; (ii) $1.5 - x$, $-1/2 + y$, $1/2 - z$. (i) $1 - x$, $2 - y$, $-z$;(ii) $1.5 - x$, $-1/2 + y$, $1/2 - z$;(iii) $1.5 - x$, $1/2 + y$, $1/2 - z$; (iv) x, $-1 + y$, z.

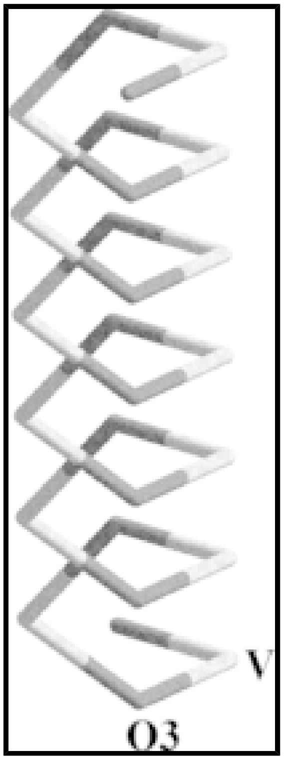


Fig. 2. View of the 1-D helical vanadate chain of 1.

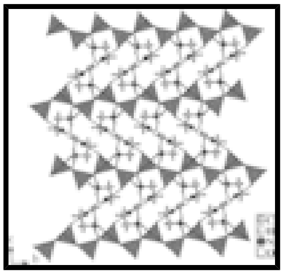


Fig. 3. Packing diagram of the title compound.

catena-poly[*N*,*N*'-bis(2-ammonioethyl)oxamide [dioxidovanadate-μ-oxido-dioxidovanadate-μ-oxido]],

Crystal data

$(C_6H_{16}N_4O_2)[V_2O_6]$

$M_r = 374.11$

Monoclinic, $P2_1/n$

$F_{000} = 380$

$D_x = 1.869$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Hall symbol: -P 2yn

a = 6.7453 (3) Å

b = 5.50870 (10) Å

c = 18.1775 (2) Å

β = 100.114 (3)°

V = 664.94 (3) Å^3

Z = 2

Cell parameters from 4832 reflections

θ = 3.1–26.0°

μ = 1.45 mm^{-1}

T = 295 (2) K

Block, brown

0.20 × 0.12 × 0.08 mm

Data collection

Siemems SMART CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 295(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

T_{min} = 0.760, T_{max} = 0.893

4832 measured reflections

1300 independent reflections

1217 reflections with $I > 2\sigma(I)$

R_{int} = 0.025

θ_{max} = 26.0°

θ_{min} = 3.1°

$h = -8 \rightarrow 8$

$k = -6 \rightarrow 6$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.029

$wR(F^2)$ = 0.078

S = 1.11

1300 reflections

91 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.6776P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}}$ = 0.34 e Å^{-3}

$\Delta\rho_{\text{min}}$ = −0.36 e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
V	0.65928 (5)	0.70817 (7)	0.20100 (2)	0.01778 (15)
O1	0.7174 (3)	0.6053 (4)	0.12407 (10)	0.0363 (5)
O2	0.4226 (3)	0.7879 (4)	0.18675 (13)	0.0411 (5)
O3	0.8179 (3)	0.9687 (3)	0.23015 (10)	0.0291 (4)
O4	0.2428 (2)	0.9303 (3)	−0.01377 (9)	0.0256 (4)
C1	0.3990 (3)	1.0441 (4)	0.00875 (12)	0.0188 (5)
C2	0.2333 (4)	1.3726 (5)	0.06245 (14)	0.0263 (5)
H2A	0.1252	1.3422	0.0207	0.032*
H2B	0.2613	1.5454	0.0635	0.032*
C3	0.1615 (4)	1.3043 (5)	0.13401 (15)	0.0295 (6)
H3A	0.2711	1.3257	0.1758	0.035*
H3B	0.0530	1.4122	0.1413	0.035*
N1	0.4117 (3)	1.2438 (4)	0.04932 (11)	0.0217 (4)
H1A	0.5286	1.2992	0.0685	0.026*
N2	0.0899 (3)	1.0505 (4)	0.13286 (11)	0.0242 (4)
H2C	0.0491	1.0172	0.1757	0.036*
H2D	0.1898	0.9508	0.1271	0.036*
H2E	−0.0123	1.0308	0.0951	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V	0.0180 (2)	0.0148 (2)	0.0203 (2)	0.00000 (14)	0.00284 (15)	0.00046 (14)
O1	0.0497 (12)	0.0343 (11)	0.0263 (9)	−0.0053 (9)	0.0105 (8)	−0.0082 (8)
O2	0.0227 (10)	0.0353 (11)	0.0626 (14)	0.0066 (8)	0.0002 (9)	0.0068 (10)
O3	0.0342 (10)	0.0222 (9)	0.0330 (9)	−0.0085 (7)	0.0114 (8)	−0.0084 (7)
O4	0.0181 (8)	0.0257 (9)	0.0326 (9)	−0.0039 (7)	0.0033 (7)	−0.0019 (7)
C1	0.0182 (11)	0.0218 (11)	0.0165 (10)	−0.0002 (9)	0.0033 (8)	0.0035 (9)
C2	0.0281 (13)	0.0201 (12)	0.0318 (13)	0.0038 (10)	0.0084 (10)	0.0004 (10)
C3	0.0307 (14)	0.0276 (14)	0.0329 (14)	0.0015 (10)	0.0131 (11)	−0.0058 (11)
N1	0.0183 (10)	0.0224 (10)	0.0248 (10)	−0.0021 (8)	0.0052 (8)	−0.0030 (8)
N2	0.0178 (10)	0.0311 (11)	0.0244 (10)	0.0023 (8)	0.0056 (8)	0.0028 (8)

Geometric parameters (Å, °)

V—O1	1.6197 (18)	C2—H2A	0.9700
V—O2	1.6322 (19)	C2—H2B	0.9700
V—O3$^{\rm i}$	1.8063 (17)	C3—N2	1.478 (3)
V—O3	1.8127 (17)	C3—H3A	0.9700
O4—C1	1.232 (3)	C3—H3B	0.9700
C1—N1	1.319 (3)	N1—H1A	0.8600
C1—C1$^{\rm ii}$	1.532 (4)	N2—H2C	0.8900
C2—N1	1.452 (3)	N2—H2D	0.8900
C2—C3	1.513 (3)	N2—H2E	0.8900

O1—V—O2	109.60 (11)	N2—C3—C2	112.1 (2)
O1—V—O3^{i}	109.79 (9)	N2—C3—H3A	109.2
O2—V—O3^{i}	105.57 (10)	C2—C3—H3A	109.2
O1—V—O3	108.03 (9)	N2—C3—H3B	109.2
O2—V—O3	110.13 (9)	C2—C3—H3B	109.2
O3^{i}—V—O3	113.68 (3)	H3A—C3—H3B	107.9
V^{iii}—O3—V	139.01 (10)	C1—N1—C2	121.7 (2)
O4—C1—N1	125.3 (2)	C1—N1—H1A	119.2
O4—C1—C1^{ii}	120.6 (3)	C2—N1—H1A	119.2
N1—C1—C1^{ii}	114.1 (2)	C3—N2—H2C	109.5
N1—C2—C3	114.8 (2)	C3—N2—H2D	109.5
N1—C2—H2A	108.6	H2C—N2—H2D	109.5
C3—C2—H2A	108.6	C3—N2—H2E	109.5
N1—C2—H2B	108.6	H2C—N2—H2E	109.5
C3—C2—H2B	108.6	H2D—N2—H2E	109.5
H2A—C2—H2B	107.5		

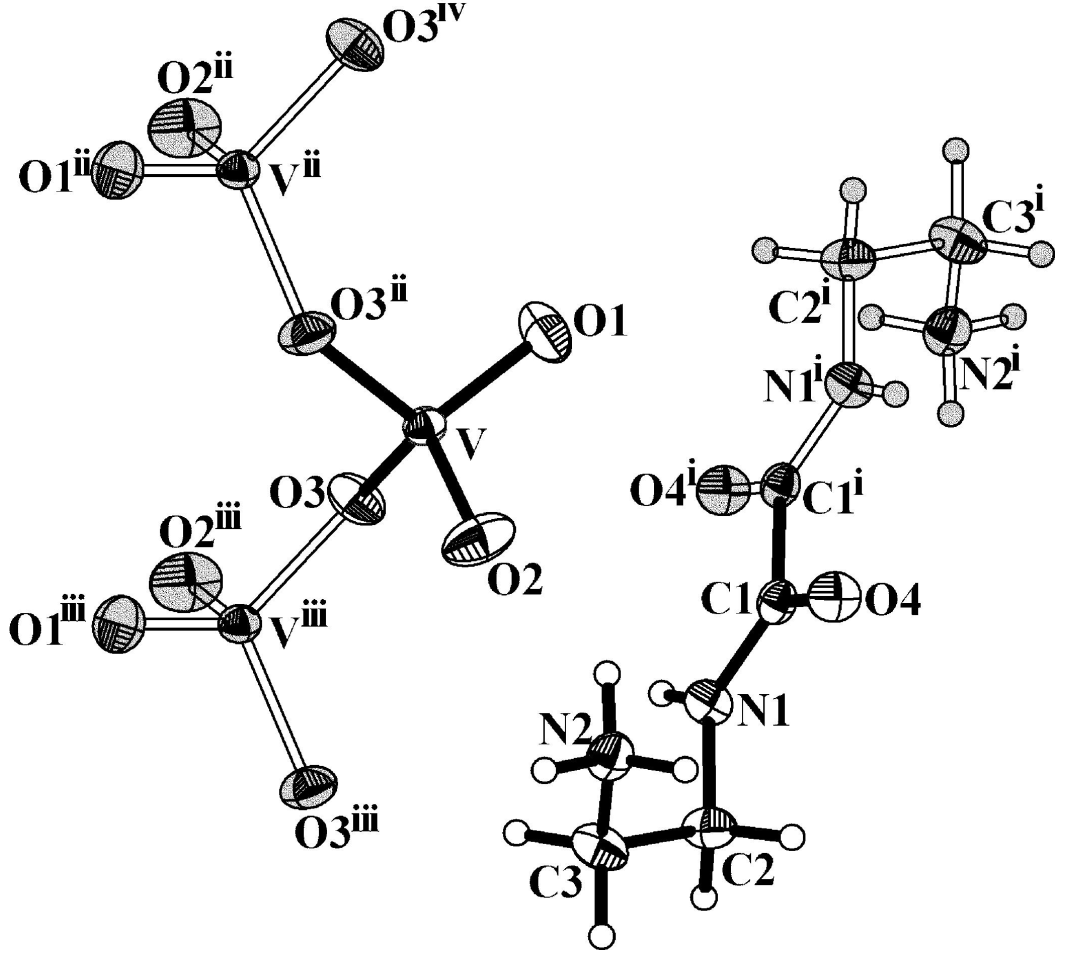
Symmetry codes: (i) $-x+3/2, y-1/2, -z+1/2$; (ii) $-x+1, -y+2, -z$; (iii) $-x+3/2, y+1/2, -z+1/2$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1^{iv}	0.86	2.24	3.013 (3)	149
N2—H2C···O3^{v}	0.89	2.01	2.799 (3)	148
N2—H2E···O4^{vi}	0.89	1.96	2.833 (3)	167
N2—H2D···O2	0.89	1.96	2.705 (3)	140

Symmetry codes: (iv) $x, y+1, z$; (v) $x-1, y, z$; (vi) $-x, -y+2, -z$.

Fig. 1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O1ii
Vii
C3i
O3ii
O1
C2i
N1i
N2i
V
O3
O4i
C1i
O2iii
O2
C1
O4
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Viii
N1
N2
O3iii
C3
C2

Fig. 2

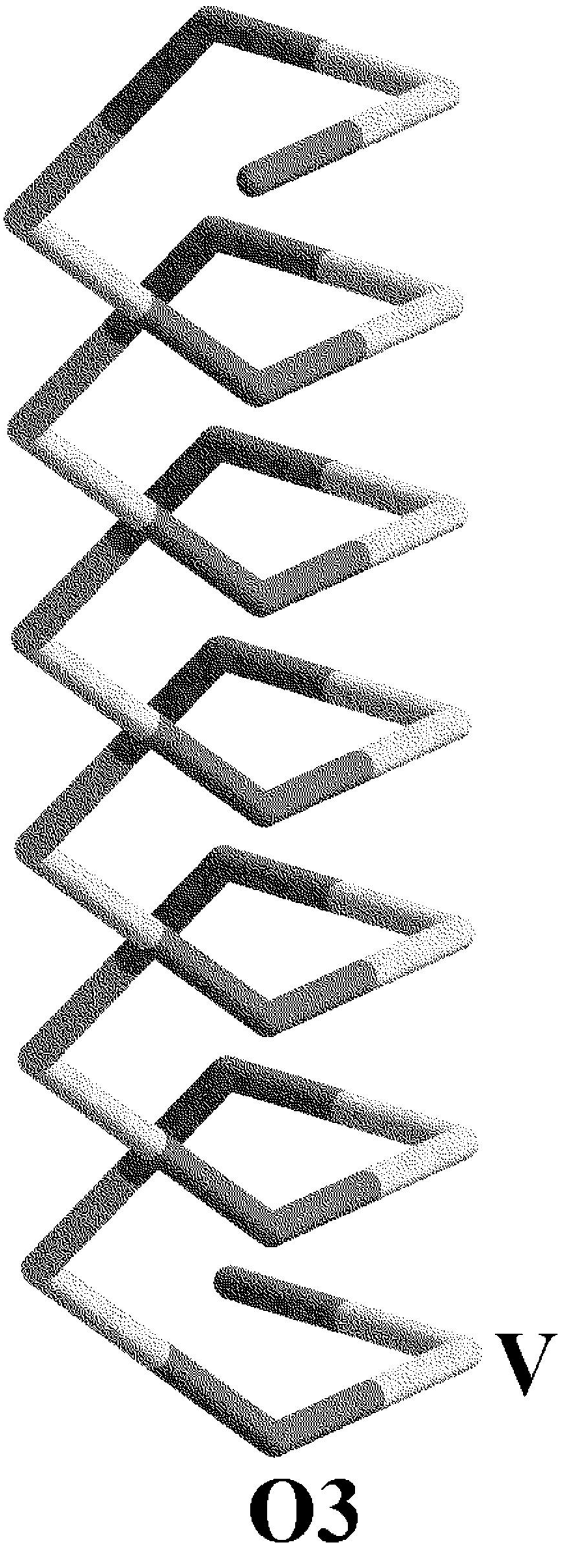

Fig. 3