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A Mononuclear Oxovanadium(IV) Complex [VO(H$_2$*L*)(SO$_4$)].5H$_2$O Derived from a Potentially Dinucleating Tetraaminodiphenol Macrocyclic Ligand (H$_2$*L*)

Soma Ghosh and Monika Mukherjee

Department of Solid State Physics,
Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700032, India

Alok K. Mukherjee

Department of Physics, Jadavpur University,
Calcutta 700032, India

Sasankasekhar Mohanta

Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700032, India

Madeleine Helliwell

Department of Chemistry, University of Manchester,
Manchester M13 9PL, England

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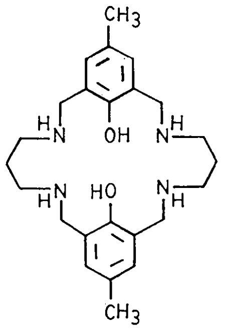
Abstract

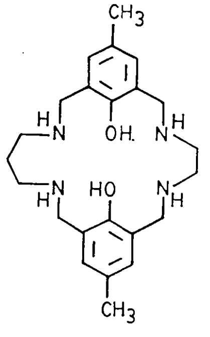
The crystal structure of {10,22-dimethyl-14,18-diaza-3,6-diazoniatricyclo[18.3.1.1^{8,12}]pentacosa-1(24),8(25),9,11,20,22-hexaene-24,25-diolate-*N*^{14},*N*^{18},*O*,*O'*}oxo(sulfato-*O*)vanadium(IV) pentahydrate, [VO(SO$_4$)(C$_{23}$H$_{34}$N$_4$O$_2$)].5H$_2$O, has been studied by single-crystal X-ray diffraction in order to determine the coordination geometry around the metal centre. The two secondary N and two phenolate O atoms from the macrocycle (which, overall, is neutral) define the equatorial plane, and the oxo and one sulfate O atom at the axial sites complete the distorted octahedral arrangement around the V atom. The crystal packing is stabilized by an extensive network of intra- and intermolecular hydrogen bonds, involving the macrocycle, SO$_4^{2-}$ and the lattice water molecules.

Comment

Macrocyclic complexes of transition metals, especially of vanadium, are of fundamental interest because of their ability to model biological phenomena (Cotton & Czuchajowska, 1990). The coordination geometry around the metal centre in these complexes depends to a great extent on the size of the metal ion with respect to the cavity of the macrocycle (Hancock, Dobson, Evers, Wade, Ngwenya, Boeyens & Wainwright, 1988; Henrick, Lindoy, McPartlin, Tasker & Wood, 1984; Nanda, Das, Venkatsubramanian, Paul & Nag, 1993). Studies with the symmetric macrocyclic ligand (H$_2$*L*^{1}), which contains two —NH(CH$_2$)$_3$NH— moieties, leading to the formation of both mononuclear [VO(H$_2$*L*^{1})(SO$_4$)].3H$_2$O and dinuclear [(VO)$_2$*L*^{1}(μ-SO$_4$)].MeOH.3H$_2$O complexes, have been reported along with the structure of the latter (Das, Nanda, Mukherjee, Mukherjee, Helliwell & Nag, 1993). In view of the unusual composition of the mononuclear oxovanadium(IV) complex of H$_2$*L*^{1} and as a result of the lack of availibility of suitable single crystals, it was of interest to determine the structure of a similar analogue. The reaction of H$_2$*L* with vanadium(IV) sulfate under the same reaction conditions used for H$_2$*L*^{1} specifically affords the mononuclear complex of composition [VO(H$_2$*L*)(SO$_4$)].5H$_2$O.



H$_2$*L*^{1}



H$_2$*L*

An *ORTEP*II (Johnson, 1976) view of the title compound with atom-labelling scheme is shown in Fig. 1. The coordination polyhedron of the V atom is a distorted octahedron with an equatorial plane formed by two secondary amine N donor atoms and two phenolate O atoms from the macrocycle; the oxo and one sulfate O atom are in the axial sites. The V atom is displaced towards the vanadyl O atom by 0.283 (2) Å from the equatorial plane, the maximum in-plane deviation being 0.033 (6) Å for N2. The distortion of the V centre from a regular octahedral geometry is reflected in the *cisoid* angles, which vary between 79.5 (2) and 103.7 (2)°, and the *transoid* angles, lying between 161.9 (2) and 172.5 (2)°. The solid angles 334.2 (5) and 334.9 (5)° at the N1 and N2 centres, respectively, indicate considerable pyramidal distortions of these atoms. The V=O distance [V=O1 1.602 (5) Å] lies within the range reported for oxovanadium(IV) complexes (Nugent & Mayer, 1988). The equatorial V—O distances [average 1.970 (5) Å] are normal. The observed V—O4 distance [2.255 (5) Å] is rather long, indicating the significant *trans* influence of the vanadyl group. Similar lengthening of the V—O(sulfate) distance *trans* to a vanadyl group is reported in the literature (Das, Nanda, Mukherjee, Mukherjee, Helliwell & Nag, 1993). The

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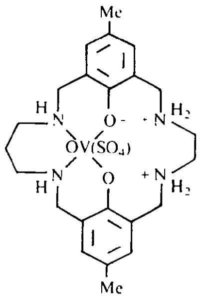
phenyl rings are essentially planar [maximum deviation at C7 = 0.033 (6) Å] and inclined to each other by 11.4 (1)°. The two uncoordinated secondary amine N atoms belonging to the smaller cavity formed by the —NH(CH$_2$)$_2$NH— moiety are protonated, resulting in the complex molecule as a whole being electrically neutral.



$[VO(H_2L)(SO_4)]$

There are several intramolecular hydrogen bonds (Table 3) which control the overall macrocycle conformation. The crystal packing (Fig. 2) is stabilized by an extensive network of hydrogen bonds involving the —NH(CH$_2$)$_2$NH— group of the macrocycle, the SO_4^{2-} ligand and the lattice water molecules. Table 3 lists 14 such D—H$\cdots$$A$ (D = donor, A = acceptor) distances and the symmetry relations between the donors and acceptors.

Experimental

Crystal data

$[VO(SO_4)(C_{23}H_{34}N_4O_2)]$.-$5H_2O$
$M_r = 651.62$
Monoclinic
$P2_1/c$
$a = 12.18\ (1)$ Å
$b = 12.16\ (1)$ Å
$c = 20.58\ (1)$ Å
$\beta = 101.46\ (6)°$
$V = 2987.3\ (38)$ Å^3
$Z = 4$
$D_x = 1.45$ Mg m^{-3}
$D_m = 1.46$ Mg m^{-3}
D_m measured by flotation in benzene–CCl$_4$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 10$–$15°$
$\mu = 4.004$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.20 × 0.17 × 0.10 mm
Brown
Crystal source: diffusion of diethyl ether into a methanol solution of the title compound

Data collection

AFC-5*R* diffractometer
2θ–ω scans
Absorption correction: empirical
$T_{min} = 0.853$, $T_{max} = 1.000$
4689 measured reflections
4451 independent reflections
3018 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0622$
$\theta_{max} = 60.21°$
$h = 0 \rightarrow 13$
$k = -1 \rightarrow 13$
$l = -23 \rightarrow 22$
3 standard reflections monitored every 150 reflections
intensity variation: 4.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0705$
$wR(F^2) = 0.1487$
$S = 1.050$
4396 reflections
458 parameters
H atoms isotropic
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 18.2674P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.165$
$\Delta\rho_{max} = 0.461$ e Å^{-3}
$\Delta\rho_{min} = -0.784$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

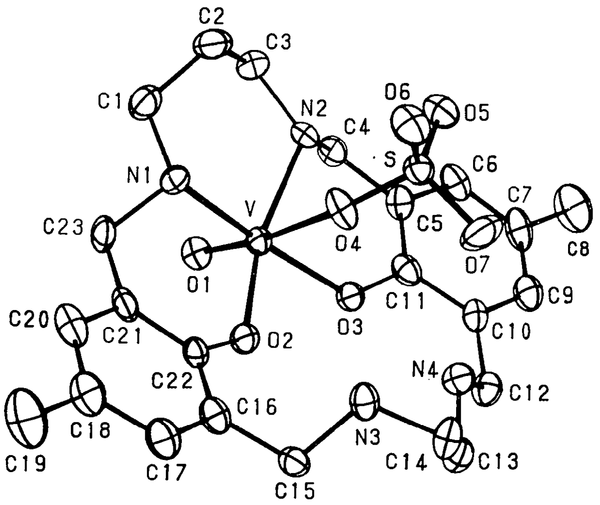


Fig. 1. *ORTEP*II (Johnson, 1976) view of the molecule showing the atom-labelling scheme.

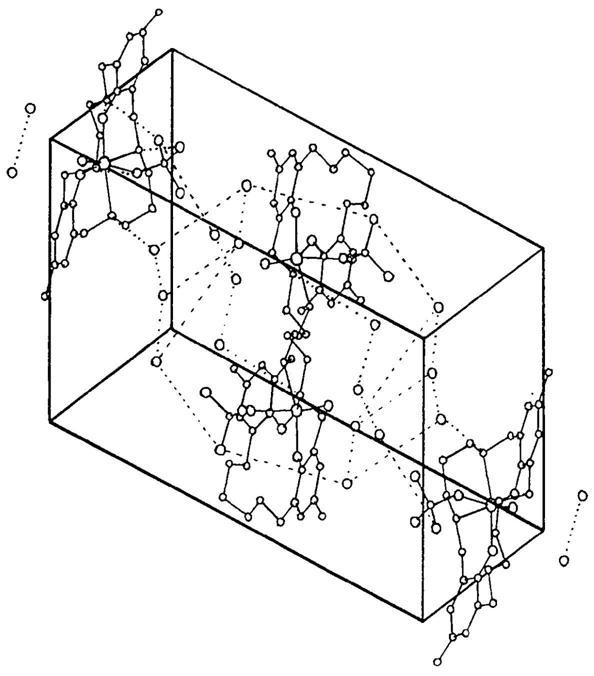


Fig. 2. Packing diagram showing intermolecular interactions.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
V	0.10923 (10)	0.22002 (10)	0.92884 (6)	0.0290 (3)
S	−0.02296 (15)	0.18957 (15)	0.75770 (9)	0.0347 (5)
O1	0.1658 (4)	0.2644 (4)	1.0010 (2)	0.0390 (12)
O2	0.1044 (4)	0.0593 (4)	0.9407 (2)	0.0348 (12)
O3	−0.0508 (4)	0.2181 (4)	0.9330 (2)	0.0336 (11)
O4	0.0497 (4)	0.1656 (4)	0.8229 (2)	0.0467 (14)
O5	−0.0460 (4)	0.3091 (4)	0.7535 (2)	0.0446 (13)
O6	0.0335 (5)	0.1581 (4)	0.7046 (2)	0.0490 (14)
O7	−0.1281 (5)	0.1302 (5)	0.7533 (3)	0.063 (2)
N1	0.2683 (5)	0.1990 (5)	0.9013 (3)	0.0331 (14)
N2	0.0827 (5)	0.3805 (5)	0.8865 (3)	0.0341 (14)
N3	−0.0357 (5)	−0.0922 (5)	0.8495 (3)	0.0353 (14)
N4	−0.2016 (5)	0.0771 (5)	0.8770 (3)	0.0385 (15)
C1	0.3333 (7)	0.3003 (7)	0.8978 (4)	0.046 (2)
C2	0.2679 (7)	0.3854 (7)	0.8520 (5)	0.048 (2)
C3	0.1826 (7)	0.4469 (7)	0.8822 (4)	0.045 (2)
C4	0.0130 (6)	0.4468 (6)	0.9235 (4)	0.039 (2)
C5	−0.1056 (6)	0.4071 (6)	0.9163 (4)	0.036 (2)
C6	−0.1904 (7)	0.4844 (6)	0.9067 (4)	0.046 (2)
C7	−0.3035 (7)	0.4536 (7)	0.9015 (4)	0.051 (2)
C8	−0.3936 (9)	0.5413 (9)	0.8942 (6)	0.079 (3)
C9	−0.3263 (6)	0.3440 (7)	0.9006 (4)	0.043 (2)
C10	−0.2441 (6)	0.2639 (6)	0.9098 (3)	0.034 (2)
C11	−0.1306 (6)	0.2960 (6)	0.9194 (3)	0.034 (2)
C12	−0.2739 (6)	0.1458 (7)	0.9113 (4)	0.039 (2)
C13	−0.2159 (6)	−0.0425 (6)	0.8838 (4)	0.039 (2)
C14	−0.1615 (6)	−0.1040 (7)	0.8357 (4)	0.041 (2)
C15	0.0211 (6)	−0.1471 (6)	0.9139 (4)	0.035 (2)
C16	0.1439 (6)	−0.1246 (6)	0.9217 (3)	0.034 (2)
C17	0.2180 (7)	−0.2096 (7)	0.9181 (4)	0.044 (2)
C18	0.3329 (6)	−0.1890 (7)	0.9249 (4)	0.044 (2)
C19	0.4140 (8)	−0.2802 (8)	0.9218 (5)	0.069 (3)
C20	0.3673 (7)	−0.0814 (7)	0.9335 (4)	0.045 (2)
C21	0.2950 (6)	0.0056 (6)	0.9376 (3)	0.033 (2)
C22	0.1804 (6)	−0.0177 (6)	0.9337 (3)	0.031 (2)
C23	0.3384 (6)	0.1211 (6)	0.9479 (4)	0.039 (2)
O*W*1	0.2565 (5)	0.1098 (5)	0.7576 (3)	0.069 (2)
O*W*2	0.7242 (5)	0.1236 (5)	0.2447 (3)	0.070 (2)
O*W*3	0.4611 (6)	0.2123 (8)	0.7658 (5)	0.115 (3)
O*W*4	0.6416 (5)	0.0964 (6)	0.7473 (3)	0.079 (2)
O*W*5	0.4826 (6)	0.0829 (8)	0.2070 (5)	0.120 (3)

Table 2. *Selected geometric parameters* (Å, °)

V—O1	1.602 (5)	N2—C4	1.485 (9)
V—O3	1.968 (5)	N3—C14	1.509 (9)
V—O2	1.972 (5)	N3—C15	1.521 (9)
V—N2	2.135 (6)	N4—C13	1.474 (10)
V—N1	2.139 (6)	N4—C12	1.489 (9)
V—O4	2.255 (5)	C1—C2	1.517 (11)
S—O6	1.454 (5)	C2—C3	1.510 (12)
S—O7	1.458 (6)	C4—C5	1.502 (10)
S—O5	1.479 (6)	C7—C8	1.516 (11)
S—O4	1.483 (5)	C10—C12	1.483 (11)
O2—C22	1.344 (8)	C13—C14	1.496 (11)
O3—C11	1.346 (8)	C15—C16	1.498 (10)
N1—C1	1.474 (10)	C18—C19	1.496 (11)
N1—C23	1.489 (9)	C21—C23	1.501 (11)
N2—C3	1.478 (10)		
O1—V—O3	102.2 (2)	C4—N2—V	110.1 (4)
O1—V—O2	103.7 (2)	C14—N3—C15	113.0 (6)
O3—V—O2	85.9 (2)	C13—N4—C12	114.7 (6)
O1—V—N2	94.2 (2)	N1—C1—C2	112.3 (6)
O3—V—N2	87.6 (2)	C3—C2—C1	113.6 (7)
O2—V—N2	161.9 (2)	N2—C3—C2	113.3 (7)
O1—V—N1	92.3 (2)	N2—C4—C5	114.3 (6)
O3—V—N1	165.3 (2)	C11—C5—C4	121.5 (6)
O2—V—N1	88.0 (2)	C6—C5—C4	118.2 (7)
N2—V—N1	94.2 (2)	C9—C7—C8	123.1 (8)
O1—V—O4	172.5 (2)	C6—C7—C8	119.8 (8)
O3—V—O4	84.7 (2)	C9—C10—C12	120.7 (7)
O2—V—O4	79.5 (2)	C11—C10—C12	120.1 (6)
N2—V—O4	83.1 (2)	O3—C11—C5	122.6 (7)
N1—V—O4	81.0 (2)	O3—C11—C10	118.8 (6)
O6—S—O7	111.4 (4)	C10—C12—N4	111.3 (6)
O6—S—O5	109.1 (3)	N4—C13—C14	110.8 (7)
O7—S—O5	109.2 (4)	C13—C14—N3	113.3 (6)
O6—S—O4	110.0 (3)	C16—C15—N3	106.5 (6)
O7—S—O4	108.5 (3)	C22—C16—C15	118.1 (6)
O5—S—O4	108.6 (3)	C17—C16—C15	120.4 (7)
C22—O2—V	129.7 (4)	C20—C18—C19	121.6 (8)
C11—O3—V	131.5 (4)	C17—C18—C19	121.2 (8)
S—O4—V	146.8 (3)	C20—C21—C23	120.7 (7)
C1—N1—C23	108.5 (6)	C22—C21—C23	120.9 (6)
C1—N1—V	115.9 (5)	O2—C22—C16	118.1 (6)
C23—N1—V	109.8 (4)	O2—C22—C21	123.3 (6)
C3—N2—C4	107.2 (6)	N1—C23—C21	111.3 (6)
C3—N2—V	117.6 (5)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	H···*A*	*D*···*A*	*D*—H···*A*
N1	HN1	O*W1*	2.227 (7)	3.127 (9)	164.9 (5)
N2	HN2	O5	2.115 (5)	3.001 (7)	159.7 (4)
N3	HN3A	O4	2.510 (6)	3.382 (8)	163.4 (4)
N4	HN4A	O7	2.178 (7)	2.933 (9)	140.7 (5)
N4	HN4B	O3	1.877 (4)	2.609 (7)	136.5 (5)
O*W*4	H*W*4A	O*W3*	1.800 (8)	2.702 (11)	151.7 (6)
O*W*5	H*W*5A	O*W*2	2.141 (7)	2.932 (10)	136.6 (6)
C13	H13A	O*W*5$^{\rm i}$	2.591 (51)	3.446 (11)	152 (4)
N4	HN4A	O*W*4$^{\rm ii}$	2.224 (6)	2.967 (9)	139.2 (5)
O*W*1	H*W*1A	O*W*2$^{\rm iii}$	1.947 (7)	2.849 (10)	142.4 (5)
O*W*5	H*W*5B	O*W*4$^{\rm iii}$	2.095 (7)	2.915 (12)	140.1 (6)
O*W*2	H*W*2A	O7$^{\rm iv}$	2.719 (6)	3.478 (9)	139.8 (5)
O*W*3	H*W*3B	O*W*5$^{\rm v}$	2.007 (10)	2.803 (14)	137.0 (6)
O*W*4	H*W*4B	O7$^{\rm vi}$	1.933 (6)	2.812 (9)	139.6 (5)

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

Data collection, cell refinement and data reduction were performed using AFC-5*R* software. The structure was solved by interpretation of a Patterson synthesis (*SHELX*76; Sheldrick, 1976) which yielded the position of the V atom. The positions of the remaining non-H atoms, including those of the solvent molecules, were obtained by successive weighted Fourier syntheses (*MULTAN*88; Debaerdemaeker, Germain, Main, Refaat, Tate & Woolfson, 1988). All non-H atoms were refined anisotropically by full-matrix least-squares on F^2 using *SHELXL*93 (Sheldrick, 1993). H atoms were positioned geometrically at calculated positions excepting those of solvent molecules which were located from difference Fourier maps. H atoms excepting those belonging to N atoms, methyl groups and solvent molecules were refined isotropically. All calculations were performed using a VAX3400 computer at the Computer Center, Indian Association for the Cultivation of Science. Geometric calculations were performed using *PARST* (Nardelli, 1983). Molecular graphics were prepared using *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978) in *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The material for publication was produced using *SHELXL*93.

The authors thank Professor K. Nag for helpful discussion.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*o*-methoxyphenyl)tin Dibromide

JENNIFER-NICOLA ROSS AND JAMES WARDELL

Department of Chemistry, University of Aberdeen,
Meston Walk, Aberdeen AB9 2UE, Scotland

GEORGE FERGUSON

Department of Chemistry and Biochemistry,
University of Guelph, Guelph, Ontario,
Canada N1G 2W1

JOHN N. LOW

Department of Applied Physics and Electronic and
Manufacturing Engineering, University of Dundee,
Dundee DD1 4HN, Scotland

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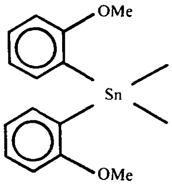
Abstract

The Sn atom in the title compound, [$SnBr_2(C_7H_7O)_2$], has a distorted tetrahedral coordination geometry. There are indications of weak Sn···O intramolecular interactions.

Comment

A recent crystal structure determination of tris(*o*-methoxyphenyl)tin iodide (Howie, Ross, Wardell & Low, 1994) provided some evidence of weak Sn···O intramolecular coordination; the shortest Sn···O1 distance was 2.965 (7) Å with an I—Sn···O1 angle of 152.1 (1)°.

The crystal structure of the title compound, (I), has now been determined. The Sn···O intramolecular separations [2.90 (1) and 2.92 (1) Å] provide indications of weak tin–oxygen coordinations. The constraints of the *ortho*-disubstituted aryl system result in the four-membered chelate rings being highly strained. Of interest, there are significant differences between the valency angles Sn1—C1*A*—C2*A* and Sn1—C1*A*—C6*A* [114.2 (6) and 125.9 (6)°, respectively], and Sn1—C1*B*—C2*B* and Sn1—C1*B*—C6*B* [114.9 (6) and 124.9 (6)°, respectively]; these values allow the Sn atom to approach each of the two O atoms more closely. The differences in the exocyclic valency angles involving each of the O atoms and the aryl-ring C atoms are generally found in methoxyaryl compounds (Howie, Ross, Wardell & Low, 1994), and so cannot be used to confirm tin–oxygen interactions.



(I)

The Sn—Br bond lengths in the present study [2.480 (2) and 2.481 (2) Å], are much shorter than those found for the distorted octahedral bis(*C*,*N*)-chelate complex bis(8-dimethylamino-1-naphthyl)tin dibromide [2.610 (2) and 2.623 (2) Å; Jastrzebski, 1991]. The C—

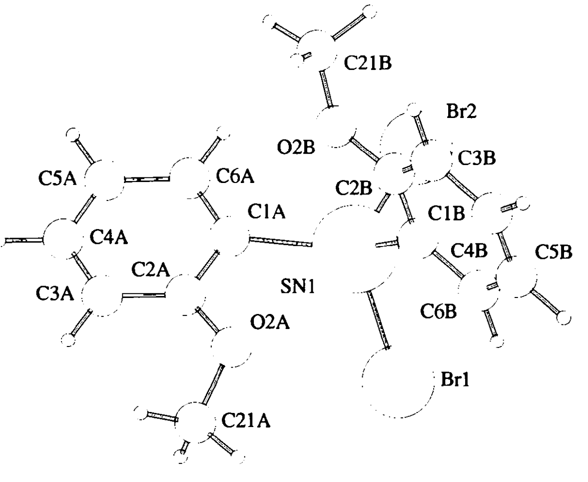


Fig. 1. Perspective view of the molecule.

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