Data collection was perfromed using *CAD*-4 *Software* (Enraf–Nonius, 1989). Lorentz–polarization corrections were applied to both sets of data. The S atom in (I) was located by the heavy-atom method and the remaining part of the structure by subsequent difference Fourier syntheses. The structure was refined by a full-matrix least-squares method with anisotropic displacement parameters for all non-H atoms. The U atom in (II) was located by the heavy-atom method and the remaining part of the structure by subsequent difference Fourier syntheses. The structure was refined by a full-matrix least-squares method with anisotropic displacement parameters for U and the atoms of the trifluoromethanesulfonate moiety (except C). Due to the pseudo-centrosymmetry of the macrocycle, strong correlations were present between atoms that would be equivalent in the centrosymmetric space group *Cmcm*. This could only be overcome by fixing constraints of equality on the corresponding displacement parameters. The two enantiomorphs were checked but gave the same results. All calculations were performed on a VAX4200 computer. Programs used: *MolEN* (Fair, 1990) and *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: PA1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Lasalocid Sodium Salts

XIUQI SHUI AND DRAKE S. EGGLESTON

SmithKline Beecham Pharmaceuticals, 709 Swedeland Road, King of Prussia, PA 19406, USA

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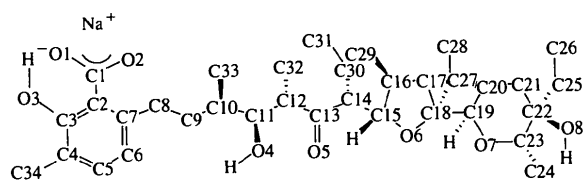
Abstract

The structures of two new forms of lasalocid sodium salt, sodium 6-[7*R*-{5*S*-ethyl-5-(5*R*-ethyltetrahydro-5-hydroxy-6*S*-methyl-2*H*-pyran-2*R*-yl)tetrahydro-3*S*-methyl-2*S*-furanyl}-4*S*-hydroxy-3*R*,5*S*-dimethyl-6-oxononyl]-2-hydroxy-3-methylbenzoate (*A*), $Na^+.C_{34}H_{53}O_8^-$, and sodium 6-[7*R*-{5*S*-ethyl-5-(5*R*-ethyltetrahydro-5-hydroxy-6*S*-methyl-2*H*-pyran-2*R*-yl)tetrahydro-3*S*-methyl-2*S*-furanyl}-4*S*-hydroxy-3*R*,5*S*-dimethyl-6-oxononyl]-2-hydroxy-3-methylbenzoate diethyl ether solvate (*B*), $Na^+.C_{34}H_{53}O_8^-.C_4H_{10}O$, are reported. Form *A* exists as a 'head-to-head' dimer, while form *B* is a 'head-to-tail' dimer. Sodium is coordinated to six O atoms from the lasalocid anion in both forms, but the coordination spheres differ. Form *A* contains a bridging carbonyl O atom, but, remarkably, the carboxylate group does not coordinate to the sodium ion. In form *B*, the carbonyl O atom does not bridge but there is a direct carboxylate–sodium interaction.

Comment

The structures of sodium salts of lasalocid and a derivative have been known for almost two decades (Schmidt, Wang & Paul, 1974; Smith, Duax & Fortier, 1978). Two new forms (*A* and *B*) were obtained as we attempted to prepare other lasalocid complexes using the sodium salt as a starting material.



(I)

In both structures, the lasalocid anion adopts the usual circular intramolecularly hydrogen-bonded conformation with interactions involving O1 and O3, O2 and O4, and O8 and the carboxylate group. Both compounds *A* and *B* occur as dimers. In the 'head-to-head' dimer of *A* (Fig. 1), the dimeric nature derives from a crystallographic twofold symmetry transformation, whereas in the 'head-to-tail' dimer of *B* (Fig. 2), the dimeric complex is formed by two crystallographically independent

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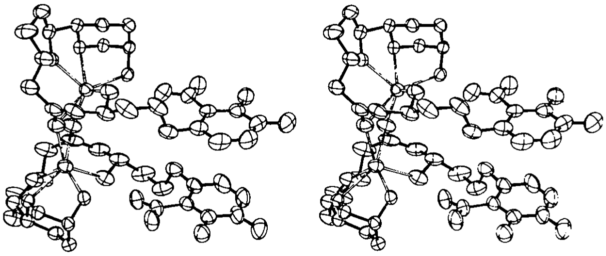

Fig. 1. Stereoscopic view of structure *A* with side chains excluded. Principal ellipsoids are drawn at the 50% probability level. The Na atoms are coordinated with unfilled bonds. Atom numbering is shown in the scheme above.

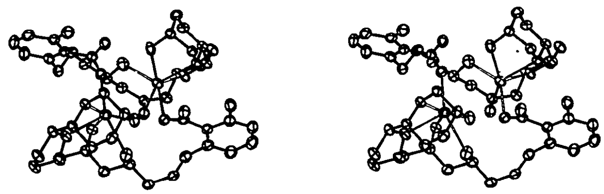

Fig. 2. Stereoscopic view of structure *B* with side chains excluded. Principal ellipsoids are drawn at the 50% probability level. The Na-atom coordination is illustrated with unfilled bonds. Atom numbering is shown in the scheme above.

molecules in the asymmetric unit. These two general dimeric forms were also observed for the sodium salt of 5-bromolasalocid (Schmidt, Wang & Paul, 1974), but the 'head-to-head' form has not been reported previously with crystallographic twofold symmetry (Duesler & Paul, 1983). Form *B* contains one molecule of diethyl ether per molecule of sodium lasalocid. Its closest contact with the lasalocid salt is 3.5 (1) Å.

In each dimer, the sodium cation is coordinated by atoms O4, O5, O6, O7 and O8. In form *A*, two Na atoms are bridged by the carbonyl atoms O5 and O5′, while in *B* the carboxylate atom O2′ provides the sixth ligand atom. In *A*, atom O2 is favorably oriented to form a seventh coordination site, but the distance of 3.81 (1) Å from Na^+ precludes a formal interaction. These arrangements of coordinating atoms are the same as those found in the structure of the sodium salt of 5-bromolasalocid (Schmidt, Wang & Paul, 1974), but different from those of the hydrated sodium salt of lasalocid reported by Smith, Duax & Fortier (1978). The Na···O distances observed for both *A* and *B* are virtually identical to analogous interactions in related structures (see Table 3). The Na···Na distance is 3.83 (1) in *A* and 3.82 (1) Å in *B*. The backbone conformations differ little between the three molecules reported here. The r.m.s. deviation from a least-squares fit between the two crystallographically independent molecules in *B* is 0.45 Å and between the molecule of *A* and one molecule of *B* is 0.50 Å. Furthermore, the similarity in backbone conformation extends to other crystal forms of this salt as evidenced by a comparison of the principal torsion angles for five related molecules (see Table 4). The general similarity in these conformations is evident and the largest range in any one torsion angle is only 20°, suggesting that the principal conformational determinant in all of these structures is coordination to the sodium ion. Moreover, different modes of coordination appear to have only localized effects on the conformation and differences in packing interactions between the crystal forms do not appear to unduly influence the shape adopted by the antibiotic.

Experimental

Form *A* crystallized from ethanol and form *B* from diethyl ether, both at room temperature.

Form *A*

Crystal data

$Na^+.C_{34}H_{53}O_8^-$
$M_r = 612.79$
Tetragonal
$P4_32_12$
$a = 12.286$ (3) Å
$c = 45.744$ (2) Å
$V = 6905$ (2) Å^3
$Z = 8$
$D_x = 1.18$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 22 reflections
$\theta = 30–31°$
$\mu = 0.741$ mm^{-1}
$T = 222$ K
Pyramidal
0.65 × 0.26 × 0.26 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
5484 measured reflections
3224 independent reflections

2297 observed reflections [$I > 3.0\sigma(I)$]
$R_{int} = 0.031$
$\theta_{max} = 62.04°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -52 \rightarrow 0$
3 standard reflections frequency: 240 min intensity decay: 2.12%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.079$
$S = 1.763$
2297 reflections
388 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0036F_o^4]$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.1699$ e Å^{-3}
$\Delta\rho_{min} = -0.1008$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Form *B*

Crystal data

$Na^+.C_{34}H_{53}O_8^-.C_4H_{10}O$
$M_r = 686.91$
Monoclinic
$P2_1$
$a = 12.90$ (1) Å
$b = 17.20$ (2) Å
$c = 17.90$ (4) Å
$\beta = 99.79$ (6)°

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 19–21°$
$\mu = 0.085$ mm^{-1}
$T = 218$ K
Rectangular

$V = 3914$ (10) Å^3	1.40 × 0.70 × 0.45 mm
$Z = 4$	Colorless
$D_x = 1.17$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.024$
ω–2θ scans	$\theta_{max} = 28.07°$
Absorption correction: none	$h = -17 \rightarrow 11$
	$k = 0 \rightarrow 22$
	$l = -23 \rightarrow 23$
18 136 measured reflections	3 standard reflections
9774 independent reflections	frequency: 240 min
7770 observed reflections [$I > 3.0\sigma(I)$]	intensity decay: 7.38%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.007$
$R = 0.044$	$\Delta\rho_{max} = 0.7633$ e Å^{-3}
$wR = 0.060$	$\Delta\rho_{min} = -0.0560$ e Å^{-3}
$S = 1.857$	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
7770 reflections	
491 parameters	
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0036F_o^4]$	

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

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

	x	y	z	U_{eq}
Na1	0.8620 (2)	0.9426 (2)	0.96103 (3)	0.080 (1)
O1	0.4740 (4)	0.7567 (3)	0.9374 (1)	0.122 (2)
O2	0.6466 (3)	0.7283 (3)	0.94504 (9)	0.107 (2)
O3	0.3412 (4)	0.6096 (4)	0.93626 (8)	0.114 (3)
O4	0.8779 (3)	0.7443 (3)	0.94911 (7)	0.104 (1)
O5	1.0206 (3)	0.8507 (4)	0.99434 (7)	0.104 (1)
O6	1.0194 (3)	0.9768 (4)	0.93323 (6)	0.100 (2)
O7	0.8344 (3)	1.0959 (3)	0.92523 (6)	0.077 (2)
O8	0.6889 (3)	0.9392 (3)	0.94190 (6)	0.072 (2)
C1	0.5515 (5)	0.6938 (4)	0.9443 (1)	0.087 (3)
C2	0.5256 (5)	0.5787 (4)	0.95226 (9)	0.083 (2)
C3	0.4168 (5)	0.5411 (5)	0.9475 (1)	0.093 (3)
C4	0.3829 (6)	0.4357 (5)	0.9530 (1)	0.109 (2)
C5	0.4629 (8)	0.3672 (5)	0.9654 (2)	0.137 (3)
C6	0.5658 (7)	0.4031 (4)	0.9718 (1)	0.132 (3)
C7	0.6017 (6)	0.5066 (4)	0.9657 (1)	0.098 (2)
C8	0.7163 (6)	0.5362 (5)	0.9733 (1)	0.105 (2)
C9	0.7927 (6)	0.5224 (6)	0.9470 (1)	0.119 (4)
C10	0.9120 (6)	0.5472 (6)	0.9526 (1)	0.135 (4)
C11	0.9312 (5)	0.6601 (5)	0.9660 (1)	0.099 (3)
C12	1.0506 (5)	0.6868 (6)	0.9674 (1)	0.112 (2)
C13	1.0723 (4)	0.8039 (6)	0.9748 (1)	0.114 (2)
C14	1.1560 (4)	0.8670 (7)	0.9571 (1)	0.132 (3)
C15	1.0995 (4)	0.8970 (7)	0.9279 (1)	0.124 (3)
C16	1.1699 (6)	0.9425 (9)	0.9037 (1)	0.188 (4)
C17	1.0849 (5)	1.0029 (7)	0.8852 (1)	0.130 (3)
C18	1.0091 (4)	1.0517 (6)	0.9085 (1)	0.108 (2)
C19	0.8888 (4)	1.0528 (5)	0.89946 (9)	0.079 (3)
C20	0.8408 (4)	0.9447 (5)	0.89097 (9)	0.082 (2)
C21	0.7176 (4)	0.9500 (4)	0.88945 (9)	0.075 (3)
C22	0.6640 (4)	1.0024 (4)	0.91591 (9)	0.068 (2)
C23	0.7177 (4)	1.1112 (4)	0.9223 (1)	0.075 (3)
C24	0.6924 (5)	1.2017 (5)	0.9008 (1)	0.093 (3)
C25	0.5416 (4)	1.0090 (4)	0.9111 (1)	0.078 (3)
C26	0.4793 (5)	1.0582 (6)	0.9369 (1)	0.100 (4)
C27	1.0485 (5)	1.1596 (7)	0.9186 (1)	0.141 (3)
C28	1.0314 (7)	1.2518 (7)	0.8964 (2)	0.184 (4)
C29	1.2317 (7)	0.856 (1)	0.8870 (1)	0.252 (4)
C30	1.2036 (6)	0.9628 (8)	0.9735 (1)	0.162 (4)
C31	1.2777 (7)	0.9308 (9)	0.9983 (2)	0.188 (4)
C32	1.1106 (6)	0.6186 (6)	0.9912 (1)	0.131 (3)
C33	0.9751 (6)	0.5341 (8)	0.9235 (2)	0.222 (4)
C34	0.2743 (7)	0.3979 (6)	0.9479 (1)	0.140 (3)

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

U_{iso} for disordered solvent atoms (values without e.s.d.'s). For others $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{iso}/U_{eq}
Na1	0.60643 (9)	0.62587 (7)	0.82081 (6)	0.0299 (5)
Na1′	0.59610 (9)	0.43462 (7)	0.71226 (6)	0.0288 (3)
O1	0.4204 (2)	0.5803 (1)	0.5942 (1)	0.036 (1)
O2	0.5838 (2)	0.5539 (1)	0.6498 (1)	0.0304 (9)
O3	0.3533 (2)	0.5136 (1)	0.4706 (1)	0.037 (1)
O4	0.6944 (2)	0.6841 (2)	0.7204 (1)	0.036 (1)
O5	0.8029 (2)	0.6004 (1)	0.8556 (1)	0.034 (1)
O6	0.6816 (2)	0.7291 (1)	0.9095 (1)	0.0308 (6)
O7	0.4743 (1)	0.6935 (1)	0.8785 (1)	0.0256 (5)
O8	0.4583 (2)	0.6720 (1)	0.7246 (1)	0.034 (1)
O1′	0.4153 (2)	0.4844 (1)	0.8939 (1)	0.035 (1)
O2′	0.5810 (2)	0.5087 (1)	0.8821 (1)	0.0311 (9)
O3′	0.3469 (2)	0.5461 (1)	1.0029 (1)	0.039 (1)
O4′	0.6877 (2)	0.3773 (1)	0.8410 (1)	0.040 (1)
O5′	0.7963 (2)	0.4556 (1)	0.7283 (1)	0.035 (1)
O6′	0.6590 (1)	0.3264 (1)	0.6504 (1)	0.0288 (5)
O7′	0.4550 (1)	0.3713 (1)	0.6193 (1)	0.0255 (8)
O8′	0.4435 (2)	0.4083 (1)	0.7643 (1)	0.033 (1)
C1	0.5139 (2)	0.5583 (2)	0.5921 (2)	0.029 (1)
C2	0.5390 (2)	0.5366	0.5152 (2)	0.028 (1)
C3	0.4557 (3)	0.5130 (2)	0.4589 (2)	0.031 (1)
C4	0.4720 (3)	0.4867 (2)	0.3876 (2)	0.037 (2)
C5	0.5730 (3)	0.4876 (2)	0.3737 (2)	0.043 (2)
C6	0.6564 (3)	0.5133 (2)	0.4271 (2)	0.043 (2)
C7	0.6420 (2)	0.5376 (2)	0.4988 (2)	0.033 (1)
C8	0.7370 (2)	0.5660 (2)	0.5538 (2)	0.035 (1)
C9	0.7350 (2)	0.6538 (2)	0.5656 (2)	0.030 (1)
C10	0.8179 (2)	0.6846 (2)	0.6301 (2)	0.032 (1)
C11	0.7958 (2)	0.6576 (2)	0.7073 (2)	0.030 (1)
C12	0.8754 (2)	0.6870 (2)	0.7744 (2)	0.033 (1)
C13	0.8458 (2)	0.6621 (2)	0.8482 (2)	0.028 (1)
C14	0.8701 (2)	0.7188 (2)	0.9145 (2)	0.031 (1)
C15	0.7748 (2)	0.7738 (2)	0.9064 (2)	0.030 (1)
C16	0.7756 (3)	0.8375 (2)	0.9657 (2)	0.035 (1)
C17	0.6580 (3)	0.8537 (2)	0.9595 (2)	0.035 (1)
C18	0.6074 (2)	0.7734 (2)	0.9444 (2)	0.029 (1)
C19	0.5032 (2)	0.7740 (2)	0.8891 (2)	0.027 (1)
C20	0.5061 (3)	0.8115 (2)	0.8122 (2)	0.033 (1)
C21	0.4036 (2)	0.7982 (2)	0.7586 (2)	0.034 (1)
C22	0.3746 (2)	0.7125 (2)	0.7524 (1)	0.028 (1)
C23	0.3746 (2)	0.6786 (2)	0.8318 (2)	0.027 (1)
C24	0.2846 (2)	0.7041 (2)	0.8712 (2)	0.036 (1)
C25	0.2682 (2)	0.6983 (2)	0.7008 (2)	0.036 (2)
C26	0.2604 (3)	0.7268 (3)	0.6196 (2)	0.045 (2)
C27	0.5969 (3)	0.7313 (2)	1.0184 (2)	0.032 (1)
C28	0.5090 (3)	0.7605 (2)	1.0571 (2)	0.041 (2)
C29	0.8395 (3)	0.9087 (2)	0.9521 (2)	0.051 (1)
C30	0.8926 (3)	0.6773 (2)	0.9907 (2)	0.036 (2)
C31	0.9832 (3)	0.6180 (2)	0.9965 (2)	0.045 (2)
C32	0.9865 (3)	0.6560 (3)	0.7721 (2)	0.061 (1)
C33	0.8242 (3)	0.7729 (2)	0.6253 (2)	0.046 (2)
C34	0.3804 (3)	0.4581 (2)	0.3304 (2)	0.051 (1)
C1′	0.5080 (2)	0.5032 (2)	0.9213 (2)	0.028 (1)
C2′	0.5313 (2)	0.5208 (2)	1.0056 (2)	0.029 (1)
C3′	0.4470 (2)	0.5428 (2)	1.0408 (2)	0.033 (1)
C4′	0.4614 (3)	0.5638 (2)	1.1178 (2)	0.042 (2)
C5′	0.5615 (3)	0.5599 (2)	1.1581 (2)	0.047 (1)
C6′	0.6471 (3)	0.5358 (2)	1.1248 (2)	0.041 (2)
C7′	0.6342 (2)	0.5174 (2)	1.0494 (2)	0.031 (1)
C8′	0.7299 (2)	0.4929 (2)	1.0169 (2)	0.032 (1)
C9′	0.7320 (3)	0.4048 (2)	1.0041 (2)	0.036 (1)
C10′	0.8156 (2)	0.3759 (2)	0.9593 (2)	0.034 (1)
C11′	0.7910 (2)	0.4016 (2)	0.8765 (2)	0.029 (1)
C12′	0.8671 (2)	0.3682 (2)	0.8275 (2)	0.030 (1)

C13′	0.8337 (2)	0.3923 (2)	0.7451 (2)	0.028 (1)
C14′	0.8488 (2)	0.3329 (2)	0.6853 (2)	0.027 (1)
C15′	0.7502 (2)	0.2802 (2)	0.6777 (2)	0.029 (1)
C16′	0.7475 (2)	0.2110 (2)	0.6234 (2)	0.034 (1)
C17′	0.6283 (2)	0.1997 (2)	0.5998 (2)	0.032 (1)
C18′	0.5838 (2)	0.2824 (2)	0.5966 (2)	0.027 (1)
C19′	0.4770 (2)	0.2891 (2)	0.6227 (2)	0.026 (1)
C20′	0.4746 (2)	0.2575 (2)	0.7016 (2)	0.033 (1)
C21′	0.3730 (2)	0.2817 (2)	0.7289 (2)	0.034 (1)
C22′	0.3543 (2)	0.3695 (2)	0.7211 (2)	0.028 (1)
C23′	0.3546 (2)	0.3935 (2)	0.6393 (2)	0.027 (1)
C24′	0.2634 (2)	0.3644 (2)	0.5807 (2)	0.033 (1)
C25′	0.2521 (2)	0.3910 (2)	0.7499 (2)	0.034 (1)
C26′	0.2217 (2)	0.4771 (2)	0.7402 (2)	0.042 (2)
C27′	0.5831 (2)	0.3210 (2)	0.5191 (2)	0.031 (1)
C28′	0.4985 (3)	0.2910 (2)	0.4559 (2)	0.040 (2)
C29′	0.8062 (3)	0.1411 (2)	0.6592 (2)	0.046 (1)
C30′	0.8641 (2)	0.3716 (2)	0.6121 (2)	0.035 (1)
C31′	0.9655 (3)	0.4201 (3)	0.6227 (2)	0.050 (2)
C32′	0.9803 (3)	0.3954 (2)	0.8527 (2)	0.045 (1)
C33′	0.8267 (3)	0.2874 (2)	0.9680 (2)	0.055 (2)
C34′	0.3694 (3)	0.5908 (3)	1.1518 (2)	0.059 (2)
O17	0.0861 (2)	0.1908 (2)	0.6745 (1)	0.054 (1)
C69	0.1159 (5)	0.1842 (4)	0.8065 (2)	0.085 (2)
C70	0.1350 (3)	0.1463 (3)	0.7360 (2)	0.056 (2)
C71	0.0988 (3)	0.1589 (3)	0.6042 (2)	0.060 (2)
C72	0.0333 (4)	0.2020 (4)	0.5420 (2)	0.073 (2)
O18	0.0266 (4)	0.9245 (3)	0.6970 (3)	0.117 (1)
C73	0.0807	0.8695	0.8169	0.1773
C74	0.0028	0.9230	0.7712	0.1393
C75	0.1180	0.8980	0.6697	0.1393
C76	0.0894	0.8997	0.5820	0.1393
C73′	0.0217	0.9340	0.8308	0.1773
C74′	0.0876	0.9126	0.7706	0.1393
C75′	−0.0586	0.9606	0.6528	0.1393
C76′	−0.0585	0.9555	0.5679	0.1393

Table 3. *Comparative* Na—O *distances* (Å) *and* O—Na—O *angles* (°) *in sodium lasalocid salts*

	A	*B*[a]	*C1*[a,b]	*C2*[a,b]	*D*[a,c]
Na—O4	2.51	2.55	2.57	2.50	2.57
Na—O5	2.72	2.55	2.63	2.73	2.67[d]
Na—O6	2.35	2.43	2.49	2.38	2.41
Na—O7	2.52	2.47	2.51	2.55	2.45
Na—O8	2.30	2.42	2.49	2.29	2.64
Na—O5′	2.26			2.31	2.42[d]
Na—O2′		2.34	2.29		
Na—O(W_1)					2.41
Na—O(W_2)					2.42[e]
O4—Na—O5	70.3	71.0			67.3
O4—Na—O6	89.6	89.4			86.2
O4—Na—O7	126.6	125.1			112.9
O4—Na—O8	88.4	79.0			66.7
O5—Na—O6	77.1	73.9			75.6
O5—Na—O7	140.5	136.7			144.1
O5—Na—O8	150.5	149.1			132.7
O6—Na—O7	68.0	67.1			67.2
O6—Na—O8	123.9	113.5			111.3
O7—Na—O8	69.0	68.0			67.0
O5′—Na—O4	127.9				161.6[d]
O5′—Na—O5	73.4				103.3[d]
O5′—Na—O6	117.6				108.5[d]
O5′—Na—O7	105.1				84.9[d]
O5′—Na—O8	107.1				115.9[d]
O2′—Na—O4		140.5			
O2′—Na—O5		86.1			
O2′—Na—O6		115.3			
O2′—Na—O7		93.8			
O2′—Na—O8		114.1			

Notes: (*a*) values for *B*, *C*1, *C*2 and *D* are averages for two independent molecules and angles for *C*1 and *C*2 are not available; coordinates are not deposited; (*b*) Schmidt, Wang & Paul (1974); (*c*) Smith, Duax & Fortier (1978); (*d*) coordinated to Na1; (*e*) coordinated to Na2.

Table 4. *Principal backbone torsion angles* (°) *for sodium lasalocid salts*

E.s.d.'s are an average of 0.6 to 0.8 Å for these structures.

	A	*B*1	*B*2	*D*1	*D*2
C1—C2—C7—C8	−0.5	−4.7	−2.5	0.3	−6.7
C2—C7—C8—C9	−84.3	−70.0	−74.7	−85.8	−75.2
C7—C8—C9—C10	−178.2	170.1	170.2	174.3	176.1
C8—C9—C10—C33	−177.5	167.6	166.0	161.8	175.0
C8—C9—C10—C11	−53.6	−67.8	−68.8	−73.8	−61.3
C9—C10—C11—O4	−51.7	−59.8	−55.4	−67.2	−62.6
C9—C10—C11—C12	−172.2	−179.4	−174.9	172.5	176.7
C10—C11—C12—C13	168.8	176.9	176.6	170.4	162.9
C10—C11—C12—C32	−71.8	−63.0	−62.9	−65.4	−77.6
C11—C12—C13—O5	43.5	33.8	36.3	43.6	49.6
C11—C12—C13—C14	−133.9	−145.1	−143.2	−134.1	−128.1
C12—C13—C14—C30	−156.0	−149.9	−152.7	−148.3	−154.9
C12—C13—C14—C15	77.5	86.0	83.5	82.6	73.7
C13—C14—C15—O6	70.7	59.7	63.4	63.1	73.2
C13—C14—C15—C16	−169.2	179.6	−176.7	−178.0	−170.3
C14—C15—O6—C18	146.6	147.3	141.5	155.1	149.1
C15—O6—C18—C19	126.0	125.2	128.9	118.7	108.9
C15—O6—C18—C27	−112.6	−115.3	−111.5	−121.7	−128.4
O6—C18—C19—O7	62.8	59.7	61.1	62.2	62.6
O6—C18—C19—C20	−58.3	−61.1	−60.1	−57.2	−60.1
C18—C19—O7—C23	177.0	176.3	178.2	178.1	175.9
C18—C19—C20—C21	166.6	171.7	168.3	170.0	172.5
C19—O7—C23—C22	60.7	59.8	61.6	60.9	58.1
C19—C20—C21—C22	−48.6	−53.3	−51.6	−51.6	−54.3
C20—C21—C22—O8	−61.6	−59.9	−58.4	−65.1	−61.7
O7—C23—C22—O8	62.3	60.8	57.7	61.3	61.7
C20—C21—C22—C25	176.7	177.5	−179.5	176.1	179.7

Data were corrected for Lorentz and polarization factors and backgrounds were obtained from an analysis of the scan profile for each reflection (Blessing, Coppens & Becker, 1974). For both structures, the absolute configuration was assigned based on literature precedent.

Two diethyl ether molecules per asymmetric unit were found for compound *B*. One of them was disordered with each ethyl group occupying two sites which were positioned in a proper geometry with occupancies of 0.5 each. Non-H atoms, with the exception of atoms of the disordered ether molecule for *B*, were refined with anisotropic displacement parameters. The temperature factors of the disordered ether atoms were assigned. H atoms, except those on atoms O3, O4 and O8, were included at calculated positions (C—H 1.00 Å). Positions for H atoms involved in hydrogen bonding were located from difference Fourier maps. Isotropic temperature factors for H atoms were assigned as $1.3B_{eq}$ of the atom to which they were bonded.

For both compounds, data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *MolEN PROCESS* (Fair, 1990); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *MolEN LSFM*; molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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μ-[*N*,*N*-Bis(2-pyridylmethyl-1κ*N*)-*N'*,*N'*-bis(2-pyridylmethyl-2κ*N*)-1,3-diaminopropan-2-olato]-1κ*N*,2κ*N'*,1:2κ^2*O*-bis(dioxovanadium)(1+) Iodide Dihydrate, $[(VO_2)_2(TPHPN)]I.2H_2O$

Ademir Neves

Departamento de Química - UFSC, 88040-900 - Florianópolis, SC, Brazil

Ivo Vencato

Departamento de Física - UFSC, 88040-900 - Florianópolis, SC, Brazil

Manfredo Hörner and Herton Fenner

Departamento de Química - UFSM, 97111-900 - Santa Maria, RS, Brazil

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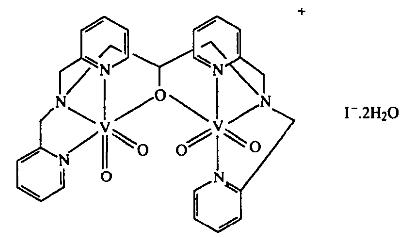
Abstract

In the binuclear $[(VO_2)_2(TPHPN)]^+$ cation of the title compound, $[V_2O_4(C_{27}H_{29}N_6O)]I.2H_2O$, the two tridentate halves of the symmetrical $TPHPN^-$ ligand are arranged so that the three donor N atoms are *fac* at one pseudo-octahedral metal centre but *mer* at the other. The strong *trans* influence of the oxo ligand is apparent from trends in the μ-V—O and V—N bond lengths.

Comment

It is well established that vanadium has an important role in many biological processes (Rehder, 1991; Butler & Carrano, 1991). In the +5 oxidation state it has been postulated that the vanadate ion acts as a potent inhibitor of Na^+, K^+ ATPase (Butler & Carrano, 1991). In order to gain more structural information about these complex systems, we synthesized and determined the crystal structure of a new binuclear vanadate complex with N and O donor ligands, (1). This is a continuation of our programme of research into the preparation and characterization of vanadium complexes with bioinorganic relevance (Neves, Ceccato, Erthal, Vencato, Nuber & Weiss, 1991; Neves, Ceccato, Vencato, Mascarenhas & Erasmus-Buhr, 1992; Neves, Ceccato, Erasmus-Buhr, Gehring, Haase, Paulus, Nascimento & Batista, 1993).



(1)

The title compound is built from discrete binuclear $[(VO_2)_2(TPHPN)]^+$ cations, uncoordinated I^- anions and water molecules of crystallization. The V atoms in the cation of (1) are in pseudo-octahedral environments, bridged by the μ-alkoxo O atom, with the VO_2 moieties in the expected *cis* configuration. The N donor atoms (from the two amine groups and the four pyridyl groups) of the symmetrical $TPHPN^-$ ligand complete the octahedral coordination spheres of the two vanadium(V) centers. The $[(VO_2)_2(TPHPN)]^+$ cation contains a $(O_2V^V—OR—V^VO_2)^+$ core, which, to the best of our knowledge, has not been crystallographically characterized previously, although a linear $(O_2V—O—VO_2)$ unit in the complex $[L_2V_2O_4(\mu\text{-}O)]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) has been reported recently (Knopp, Wieghardt, Nuber, Weiss & Sheldrick, 1990). Pertinent bridging features include the $V^V\cdots V^V$ distance of 3.690 (3) Å and the V(1)—O(5)—V(2) angle of 126.2 (1)°. Moreover, it is worth noting that the two tridentate halves (each with one amine and two pyridyl N donor atoms) of the symmetrical bridging ligand adopt distinct configurations around the vanadium centres: V(1) is coordinated in a meridional fashion whereas about V(2) the arrangement is facial.

The terminal V—O distances are short [average 1.620 (3) Å], indicating considerable multiple-bond character, and agree well with V=O distances in dimeric (Knopp *et al.*, 1990) and monomeric octahedral complexes containing *cis*-dioxovanadium units (Neves, Walz, Wieghardt, Nuber & Weiss, 1988; Neves, Hörner,

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