the initial binding of phosphate. The slow migration of ^{113}Cd(II) to the opposite B site is then observed to be a slow process with a half-time of 17 h. Likewise, only one monomer of Cu_2E_2AP binds phosphate (Figure 4), and the same migration appears to best account for all the spectroscopic data.

The initial event that prevents the second A site from binding phosphate and restoring symmetry to the dimer, prior to the metal ion migration, must be a conformational change accompanying phosphorylation of one monomer and propagated across the monomer–monomer interface. Once this conformational change has occurred, the affinities of a particular species of metal ion for the unliganded A site relative to the affinity (of the same metal ion) for the B site adjacent to a phosphorylated A site must determine whether migration of the metal ion occurs. No evidence of phosphate-induced migration has been found in the case of the Zn_2E_2AP,[24] Co_2E_2AP,[24] or Mn_2E_2AP[29] enzymes, despite the fact that only one monomer becomes phosphorylated in these species as well. On the other hand, migration appears to be induced by phosphorylation in the case of Cd_2E_2AP or phosphate binding to A-site Cu(II) in the case of Cu_2E_2AP.

Data obtained by several spectroscopic probes show that the A-site metal ion senses the presence of the B-site metal ion, despite the fact that the two sites in most cases do not appear to share a ligand. This same phenomenon can be observed in the Cu_AMg_B mixed species, as shown by the change in the ESR signal of Cu_2E_2AP when Mg(II) occupies the B site (Figure 3B). This binding of Mg(II) to the B site may actually destabilize Cu_A by distorting the A site, since the phosphate-induced migration of one of the A-site Cu(II) ions to the opposite B site occurs more rapidly in the presence of Mg(II). While not normally sharing a ligand, sites A and B do share a small section of polypeptide chain, since His-370 is ligated to the B-site metal, while His-372 is ligated to the A-site metal.[14] Thus, the two ligands are separated only by Ala-371 and a conformational change upon binding of metal ion to the B site could be propagated along this short region of the peptide chain.

It is possible that the square-planar nature of the Cu(II) complex places the phosphate ligand in an unusual position relative to the hydroxyl of Ser-102 and thus prevents phosphorylation of the enzyme. In the case of the paramagnetic derivative of alkaline phosphatase formed with four Mn(II) ions, there is no magnetic coupling between the A- and B-site metal ions[29] and the enzyme does phosphorylate Ser-102.[25]

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Registry No. AP, 9001-78-9; PO_4^{3-}, 14265-44-2; Cu, 7440-50-8.

Contribution from the Institute of Physical
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Crystal Structure of a Silver Salt of the Antibiotic Lasalocid A: A Dimer Having an Exact 2-fold Symmetry

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The crystal structure of a silver salt of the antibiotic lasalocid A, prepared from lasalocid A sodium salt and silver perchlorate in aqueous acetone, has been determined by X-ray analysis. The salt forms two types of "head-to-tail" dimers, which share a common crystallographic 2-fold rotation axis in the crystal lattice; both dimeric structures are, therefore, completely identical except for the mutual arrangement of the terminal ethyl substituents. The ionophore molecule adopts the familiar cyclic conformation with the polar oxygen groups directed toward the interior of the molecule to wrap a metal ion and the nonpolar groups toward the exterior. The metal ion is six-coordinated in the range of 2.31 (1)–2.83 (1) Å by five oxygens of one anionic molecule and a carboxylate oxygen of its pairing molecule; the metal–metal separation is 3.197 (2) Å. This is the first crystal structure in which an exact 2-fold symmetry exists in the lasalocid A dimer. Crystallographic details for $Ag^+(C_{34}H_{53}O_8)^-$: space group $C222_1$, a = 22.439 (5) Å, b = 16.976 (3) Å, c = 18.619 (4) Å, V = 7092 (3) Å^3, Z = 8. The final discrepancy factors R_F and R_{wF} are 0.053 and 0.069, respectively, for 1832 observed reflections with $F_o > 3\sigma(F_o)$.

Introduction

Since the advent[1] of lasalocid A (**1**) in 1951 as one of the first representatives of the naturally occurring ionophores, it has received much attention, especially because of its ability to transport mono-, di-, and trivalent cations across natural and artificial membranes, resulting in a large body of data on its biology[2a] and chemistry.[2b] X-ray crystallographic studies[3] of 13 lasalocid A structures, including free acids,[4] an amine salt,[5] and complexes with such metals as Na^+,[6a–c] Ag^+,[6d,e] Cs^+,[6g] and Ba^{2+},[6f] have shown that lasalocid A has a strong propensity to form dimeric structures,[4c,6b–f] in preference to monomeric[4a,b,5,6a] or polymeric[6g] ones; this is due to the relatively small molecular size of lasalocid A among acid ionophores that makes it difficult for a single anion to provide three-dimensional nonpolar protection for a metal ion in a 1:1 complex.[3] Somewhat surprisingly, of the seven dimeric

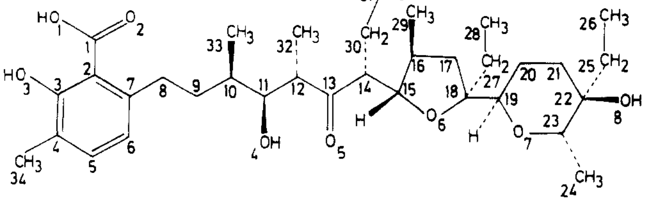

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Table I. Crystal Data and Summary of Data Collection

compd	Ag^+(lasalocid A^-)
formula	$C_{34}H_{53}O_8Ag$
fw	697.660
a, Å	22.439 (5)
b, Å	16.976 (3)
c, Å	18.619 (4)
V, Å^3	7092 (3)
Z	8
space group	$C222_1$
density, g cm^{-3}	1.307 (calcd), 1.31 (1)^a (measd)
cryst shape; dimens, mm	plate; 0.10 ({100}) × 0.32 ({010}) × 0.40 ({001})
radiation	Mo Kα (λ = 0.71073 Å) from graphite monochromator
temp, K	293
μ, cm^{-1}	6.05
scan speed, deg min^{-1}	4.0 (in 2θ)
scan range, deg	$1.6 + 0.5 \tan \theta$
scan mode	ω scan for $2\theta \leq 30°$, ω–2θ scan for $2\theta > 30°$
2θ limits, deg	3.0–50.0
bkgd counting, s	5 at the lower and upper limits of each scan
no. of unique data measd	3448
no. of unique data used ($F_o > 3\sigma(F_o)$)	1832

^{a}Measured by flotation in an aqueous zinc chloride solution.

structures, none exhibit crystallographic 2-fold symmetry, although in several cases[4c,6c,d,f] the complex has pseudo-2-fold symmetry. We report here the crystal structure of a Ag^+–lasalocid A anion (L^-) dimer that shows, for the first time, the existence of exact 2-fold symmetry relating the dimer atoms in the crystal. The complex is structurally different from two other silver salts[6d,e] but very similar to a sodium salt.[6c] An effect of the mutual arrangement of the C25–C26 ethyl groups in the dimer on the "head-to-tail" dimeric structure is emphasized in connection with its possible role in controlling the structural change, possibly a process necessary for lasalocid A functions.

Experimental Section

Preparation. The salt was prepared by mixing lasalocid A sodium salt (61 mg, 0.1 mmol; Sigma) dissolved in 10 mL of acetone and $AgClO_4$ (21 mg, 0.1 mmol; Kanto Chemical) in 10 mL of water and allowing the solution to stand at room temperature. Colorless plates formed after a few days. Anal. Calcd for $AgC_{34}H_{53}O_8$: C, 58.54; H, 7.66. Found: C, 58.58; H, 7.70.

Collection and Reduction of the X-ray Data. Cell constants were determined on a Rigaku automated diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from 20 high-order reflections ($17 < 2\theta < 23°$). Details of the crystal parameters and data collection are summarized in Table I. Three standard reflections were monitored every 100 measurements, but no deterioration was observed. The diffraction pattern was relatively weak and did not extend beyond $2\theta = 45°$ mostly due to the small crystal size and partially due to the disorder of the ethyl substituent. Intensities were corrected for Lorentz and polarization effects but not for absorption since the variation in F_o of an axial reflection, 002, at $\chi = 90°$ with the spindle angle ϕ was within 4% from the mean and calculated transmission factors[7] were 0.83–0.94.

Solution and Refinement of the Structure. The structure was solved by heavy-atom methods and refined by block-diagonal least-squares methods, minimizing the function $\sum w(F_o - |F_c|)^2$. The absolute configuration of the lasalocid A molecule was deduced from its known stereochemistry.[8] Thermal parameters of all non-hydrogen atoms were refined anisotropically, including the terminal C26 atom, which is disordered at two positions with occupancy factors of 0.7 for C26 and 0.3 for C26′, values estimated by their electron densities.[9] All 58 H atoms attached to C atoms, including disordered H atoms [H1(C25), H2(C25), H1(C26), H2(C26), and H3(C26), for which occupancy factors are 0.7, and H1(C25)′, H2(C25)′, H1(C26)′, H2(C26)′, and H3(C26)′, for which occupancy factors are 0.3], were calculated from the known stereochemistry by adopting the C–H distances[10] of 1.09 and 1.08 Å for methane-type and benzene-type bondings, respectively, while all three hydroxyl H atoms were located from a difference Fourier map. These H atom positions were not refined but included in the structure factor calculations in the final cycles of the refinement with isotropic thermal parameters fixed at 7 Å^2. Final $R = \sum ||F_o| - |F_c|| / \sum F_o$, $R_w = [\sum w(F_o - |F_c|)^2 / \sum w F_o^2]^{1/2}$, and $S = [\sum w(F_o - |F_c|)^2/(m - n)]^{1/2}$ values were 0.053, 0.069, and 3.2, respectively, for 1832 unique observed reflections (m) with $F_o > 3\sigma(F_o)$ and 397 variables (n). The weighting scheme was of the type suggested by Hughes:[11] $w = 1.0$ for $F_o \leq 100.0$ and $w^{1/2} = 100.0/F_o$ for $F_o > 100.0$. No unusual trends were observed in an analysis of either $(\sin \theta)/\lambda$ or F_o; $(\Delta/\sigma)_{max} = 0.38$ and $\Delta\rho_{max} = 0.63$ e Å^{-3} near the metal position (1.1 Å).

Table II. Atomic Positional Parameters (×10^5 for Ag and ×10^4 for Other Atoms) for Ag^+(lasalocid A^-)

	x	*y*	*z*
Ag	69174 (6)	41895 (7)	4370 (7)
O1	7946 (5)	4661 (7)	−1503 (6)
O2	6995 (5)	4807 (6)	−1270 (5)
O3	8350 (5)	5255 (6)	−2622 (6)
O4	6409 (5)	3408 (8)	−755 (6)
O5	5761 (5)	4227 (7)	427 (6)
O6	6501 (5)	2968 (6)	1102 (6)
O7	7699 (5)	3365 (6)	1138 (5)
O8	7752 (5)	3735 (7)	−317 (6)
C1	7415 (7)	4788 (8)	−1692 (8)
C2	7318 (7)	4944 (9)	−2497 (9)
C3	7795 (7)	5193 (9)	−2896 (9)
C4	7732 (8)	5409 (9)	−3637 (9)
C5	7175 (8)	5306 (11)	−3948 (10)
C6	6708 (7)	5061 (11)	−3551 (10)
C7	6753 (7)	4888 (10)	−2802 (8)
C8	6208 (7)	4604 (10)	−2428 (9)
C9	6207 (7)	3699 (10)	−2289 (9)
C10	5724 (7)	3407 (9)	−1774 (9)
C11	5848 (6)	3692 (10)	−1007 (8)
C12	5387 (6)	3377 (8)	−482 (9)
C13	5547 (7)	3593 (9)	282 (9)
C14	5443 (7)	2988 (10)	866 (9)
C15	6003 (7)	2482 (9)	899 (9)
C16	6004 (8)	1819 (9)	1452 (10)
C17	6663 (7)	1694 (9)	1590 (9)
C18	6927 (8)	2528 (8)	1538 (8)
C19	7524 (7)	2566 (10)	1121 (8)
C20	7493 (7)	2238 (8)	362 (9)
C21	8084 (8)	2410 (11)	−41 (10)
C22	8234 (7)	3282 (10)	−5 (9)
C23	8253 (7)	3543 (9)	797 (9)
C24	8780 (8)	3247 (11)	1230 (9)
C25	8826 (8)	3474 (11)	−373 (10)
C26^a	8862 (12)	3191 (19)	−1185 (21)
C26′^{a}	9078 (22)	4324 (43)	−252 (27)
C27	6950 (8)	2945 (9)	2262 (8)
C28	7443 (9)	2668 (11)	2764 (9)
C29	5670 (8)	1081 (10)	1191 (13)
C30	5278 (9)	3378 (13)	1574 (10)
C31	4706 (10)	3845 (15)	1512 (13)
C32	4762 (8)	3727 (13)	−625 (9)
C33	5681 (10)	2520 (10)	−1853 (11)
C34	8270 (9)	5702 (12)	−4037 (9)

^{a}These atoms are disordered: occupancy factors 0.7 for C26 and 0.3 for C26′.

Neutral atomic scattering factors were used with Ag corrected for anomalous dispersion.[12] All computations were carried out by using the UNICS III program system[13] on a FACOM 380 computer. The final atomic positions with the standard deviations for non-hydrogen atoms are

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Table III. Interatomic Distances (Å) and Angles (deg) for Ag$^+$(lasalocid A$^-$)

(a) Coordination Sphere							
Ag–O4	2.827 (12)	Ag–O6	2.589 (10)	Ag–O8	2.464 (11)	(Ag···Ag′)[a]	3.197 (2)
Ag–O5	2.596 (11)	Ag–O7	2.596 (10)	Ag–O2′[a]	2.310 (10)		
O4–Ag–O5	66.6 (3)	O4–Ag–O2′[a]	154.7 (4)	O5–Ag–O2′[a]	93.6 (4)	O7–Ag–O8	66.8 (4)
O4–Ag–O6	81.6 (4)	O5–Ag–O6	70.3 (4)	O6–Ag–O7	64.7 (3)	O7–Ag–O2′[a]	90.5 (3)
O4–Ag–O7	114.5 (3)	O5–Ag–O7	133.9 (4)	O6–Ag–O8	107.5 (4)	O8–Ag–O2′[a]	123.6 (4)
O4–Ag–O8	73.4 (4)	O5–Ag–O8	139.8 (4)	O6–Ag–O2′[a]	107.3 (4)		
(b) Lasalocid A Anion							
C1–C2	1.54 (2)	C8–C9	1.56 (2)	C14–C30	1.52 (3)	C19–C20	1.52 (2)
C2–C3	1.37 (2)	C9–C10	1.53 (2)	C30–C31	1.51 (3)	C20–C21	1.55 (2)
C3–C4	1.44 (2)	C10–C11	1.53 (2)	C15–C16	1.53 (2)	C21–C22	1.52 (2)
C4–C5	1.39 (3)	C10–C33	1.52 (2)	C16–C17	1.51 (2)	C22–C23	1.56 (2)
C5–C6	1.35 (3)	C11–C12	1.52 (2)	C17–C18	1.54 (2)	C23–O7	1.43 (2)
C6–C7	1.43 (2)	C11–O4	1.43 (2)	C18–O6	1.46 (2)	O7–C19	1.41 (2)
C7–C2	1.39 (2)	C12–C13	1.51 (2)	O6–C15	1.44 (2)	C22–O8	1.45 (2)
C1–O1	1.26 (2)	C12–C32	1.55 (2)	C16–C29	1.54 (2)	C22–C25	1.53 (2)
C1–O2	1.23 (2)	C13–C14	1.51 (2)	C18–C19	1.55 (2)	C25–C26	1.59 (4)
C3–O3	1.35 (2)	C13–O5	1.21 (2)	C18–C27	1.52 (2)	C25–C26′	1.57 (7)
C4–C34	1.50 (3)	C14–C15	1.52 (2)	C27–C28	1.52 (2)	C23–C24	1.52 (2)
C7–C8	1.49 (2)						
C1–C2–C3	118 (1)	C7–C8–C9	114 (1)	C14–C30–C31	112 (2)	C19–C20–C21	110 (1)
C2–C3–C4	121 (2)	C8–C9–C10	115 (1)	C14–C15–C16	116 (1)	C20–C21–C22	111 (1)
C3–C4–C5	117 (2)	C9–C10–C11	111 (1)	C15–C16–C17	103 (1)	C21–C22–C23	109 (1)
C4–C5–C6	121 (2)	C9–C10–C33	108 (1)	C16–C17–C18	104 (1)	C22–C23–O7	110 (1)
C5–C6–C7	123 (2)	C11–C10–C33	115 (1)	C17–C18–O6	105 (1)	C23–O7–C19	116 (1)
C6–C7–C2	117 (1)	C10–C11–C12	111 (1)	C18–O6–C15	111 (1)	O7–C19–C20	113 (1)
C7–C2–C1	121 (1)	C10–C11–O4	111 (1)	O6–C15–C16	104 (1)	O7–C19–C18	106 (1)
C7–C2–C3	121 (2)	C12–C11–O4	106 (1)	O6–C15–C14	109 (1)	C21–C22–O8	109 (1)
C2–C1–O1	116 (1)	C11–C12–C13	111 (1)	C15–C16–C29	113 (2)	C23–C22–O8	105 (1)
C2–C1–O2	121 (1)	C11–C12–C32	112 (1)	C17–C16–C29	115 (1)	C21–C22–C25	112 (1)
O1–C1–O2	123 (1)	C13–C12–C32	106 (1)	C17–C18–C19	114 (1)	C23–C22–C25	110 (1)
C2–C3–O3	123 (2)	C12–C13–C14	118 (1)	O6–C18–C19	105 (1)	O8–C22–C25	111 (1)
C4–C3–O3	116 (1)	C12–C13–O5	121 (1)	C17–C18–C27	113 (1)	C22–C25–C26	114 (2)
C3–C4–C34	119 (2)	C14–C13–O5	120 (1)	O6–C18–C27	106 (1)	C22–C25–C26′	116 (2)
C5–C4–C34	124 (2)	C13–C14–C15	107 (1)	C19–C18–C27	113 (1)	C22–C23–C24	116 (1)
C2–C7–C8	125 (1)	C13–C14–C30	111 (1)	C18–C27–C28	115 (1)	O7–C23–C24	112 (1)
C6–C7–C8	118 (1)	C15–C14–C30	114 (1)	C18–C19–C20	114 (1)		

[a] These atoms are symmetry-related by x, $1 - y$, $-z$, relative to the reference molecule at x, y, z.

listed in Table II. Anisotropic thermal parameters of non-hydrogen atoms and hydrogen positional parameters are given in Tables V and VI (supplementary material), respectively.

Results

Interatomic distances and angles are listed in Table III, and close contacts involving hydrogen bonds are in Table IV.

The structure consists of a discrete dimer composed of two lasalocid A anions deprotonated at the carboxyl group and two Ag$^+$ cations, as shown together with a schematic representation in Figure 1. The metal ion is coordinated to six oxygen atoms: five are from one anion molecule, the ethers O6 and O7, the hydroxyls O4 and O8, and the carbonyl O5, with Ag–O distances of 2.59 (1), 2.60 (1), 2.83 (1), 2.46 (1), and 2.60 (1) Å, respectively; the sixth position is occupied by the carboxylate O2 of the other anion molecule, which is related by a crystallographic 2-fold symmetry, with an Ag–O2 distance of 2.31 (1) Å, thus forming a dimeric structure in a "head-to-tail" fashion in which the "head" phenyl ring of one anion is opposite to the "tail" ether ring of the other. The conformational rigidity[3] of lasalocid A also holds for the present complex [torsion angles of the backbone of the molecule are in Table VII (supplementary material)]; the molecule is folded into a pseudocyclic conformation stabilized by an intramolecular "head-to-tail" hydrogen bond between the carboxylate O1 and the terminal hydroxyl O8[14] [2.75 (2) Å] and reinforced by an additional hydrogen bond between the carboxylate O2 and the inner hydroxyl O4 [2.88 (2) Å], with the polar oxygen groups directed toward the interior of the molecule and with the nonpolar groups directed toward the exterior. The ethyl substituent C25–C26 is disordered to take two positions: the C25–C26 bond bisects the C21–C22–O8 angle (type B^{3a}) [C21–C22–C25–C26 = 55 (2)°] while the C25–C26′ bond bisects the C23–C22–O8 angle (type A^{3a}) (not shown in Figure 1) [C23–C22–C25–C26′ = −49 (3)°]. However, the interatomic C26′···C26′ distance of 2.48 (9) Å within the dimer precludes the existence of a dimer involving two type A orientations (more details on this point are discussed later). The six-membered tetrahydropyran ring is in a chair form, and the five-membered ring assumes an envelope form with C16 deviating by 0.56 (3) Å from the remaining four-atom plane [torsion angle C15–O6–C18–C17 = 1 (2)°], both usual conformations in the lasalocid A structures. The carboxylate group is nearly coplanar with the phenyl ring with a slight twist toward the direction opposite to the main chain, probably due to the steric constraint between them [torsion angle C3–C2–C1–O1 = −21 (2)°]. A "salicylic acid type" hydrogen bond between H(O3) and the carboxyl O1 [O3···O1 = 2.49 (2) Å] may contribute to this coplanarity; otherwise the carboxyl group significantly rotates as exemplified in the crystal structure[16] of 2-acetoxy-6-methylbenzoic acid, in which the carboxylate group is flanked by the methyl and the acetoxy groups but, unable to form a hydrogen bond, rotates 44.7 (2)° from the benzene plane. The bond distances and angles are mostly as expected.[5,6b,f]

In the crystal lattice, dimer units are relatively loosely packed by nonpolar van der Waals contacts (Figure 2); the closest contact is 3.56 (2) Å between C3 and C17 (at $^3/_2 - x$, $^1/_2 - y$, $-^1/_2 + z$).

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(14) Although the hydroxyl O8 also makes a close contact with the carboxylate O2 [3.06 (2) Å], its participation in a "three-center" hydrogen bond with O2 remains uncertain: the H(O8)···O2 distance (2.79 Å) falls within the cutoff value of 2.85 Å,[15] but the sum of the three angles (O8–H···O1 = 143°, O8–H···O2 = 93°, and O1···H···O2 = 52°) deviates from ~360°. We thank a reviewer for leading our attention to this paper.[15]

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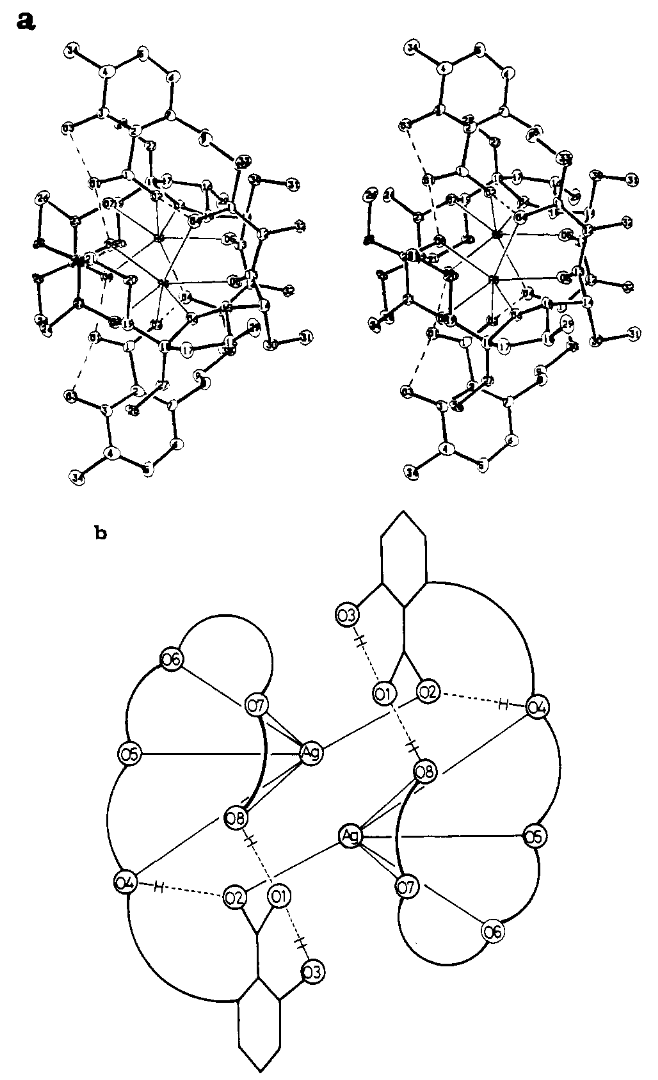

Figure 1. (a) Stereoscopic view of the Ag$^+$(lasalocid A$^-$) salt, showing a "head-to-tail" dimeric structure that has an exact 2-fold symmetry with a rotation axis being horizontal in the plane of the paper. (b) Schematic representation of the molecule in which a 2-fold rotation axis passes perpendicularly through the paper. Broken lines denote hydrogen bonds.

Table IV. Close Contacts Involving Hydrogen Bonds in Ag$^+$(lasalocid A$^-$)

A	B	equiv posn of B	A–H, Å	A···B, Å	H···B, Å	A–H···B, deg
(a) Hydrogen Bonds						
O3	O1	x, y, z	1.18	2.49 (2)	1.77	113
O4	O2	x, y, z	1.02	2.88 (2)	2.02	140
O8	O1	x, y, z	1.12	2.75 (2)	1.76	143
(b) Other Close Contacts (Less Than 3.6 Å)						
O1	O7	$x, 1-y, -z$		3.46 (2)		
O1	C23	$x, 1-y, -z$		3.39 (3)		
O2	O5	$x, 1-y, -z$		3.58 (2)		
O2	O7	$x, 1-y, -z$		3.49 (1)		
O5	O5	$x, 1-y, -z$		3.07 (2)		
O7	C1	$x, 1-y, -z$		3.36 (2)		
C3	C17	$^3/_2-x, ^1/_2-y, -^1/_2+z$		3.56 (2)		

Discussion

Comparison of the Structures of the Three Silver Salts.[6d,e] The "head-to-tail" dimer formation is common to all the three Ag$^+$ salts. However, there are distinct differences in the mutual orientations of the two lasalocid A monomers and in the metal ligation modes. The Ag$^+$(L$^-$) salt[6d] possesses a *pseudo*-2-fold symmetry in the dimer in which each Ag$^+$ ion is coordinated, on one side, to five oxygens (O4–O8) and, on the other side, to the phenyl double bond (C5 and C6) of the pairing ionophore, and the Ag–Ag separation is quite large [7.108 (2) Å]. The Ag$^+$(5-NO$_2$-L$^-$) salt[6e] forms a *less* symmetrical structure (the least symmetrical of all the seven dimers), where one Ag$^+$ ion is complexed with six oxygens, four (O5–O8) from one molecule and two (O1 and O8) from the other, while the other Ag$^+$ ion is complexed with five oxygens, four (O5–O8) from one molecule and one (O1) from the other, with the Ag–Ag separation being small [3.565 (2) Å]. On the other hand, the present Ag$^+$ salt has an *exact* 2-fold symmetry and metal ligation sites are the same as those of the Ag$^+$(L$^-$) salt[6d] except for one site from the partner anion, i.e., O2 instead of η^2-phenyl bonding, with a small Ag–Ag separation [3.197 (2) Å]. Long or short metal–metal separations in these structures are responsible for the metal bonding to the aromatic ring or carboxylate moiety of the second anion, respectively. It is noteworthy here that two different crystalline forms involving different structures, namely the orthorhombic form ($C222_1$) in the present salt and the monoclinic form ($P2_1$) in the Ag$^+$(L$^-$) salt,[6d] were obtained from the same crystallization solvent, though starting materials and their treatment were different. A similar situation is encountered in lasalocid A–methanol,[4a] even from the same starting materials, though structural differences in the two crystalline forms are not so drastic as those in the two silver salts; that is, a major difference occurs in the geometry of the C25–C26 ethyl group for lasalocid A–methanol (vide infra). The structure of the present Ag$^+$ salt is essentially the same as that of form I of the Na$^+$(5-Br-L$^-$) salt,[6c] including the hydrogen-bonding scheme, with a minor difference being a *pseudo*-2-fold symmetry in the latter.

Effect of the Arrangement of the C25–C26 Substituent on the "Head-to-Tail" Dimeric Structure. The present salt involves two kinds of anion molecules, A and B, which are disordered in the crystal lattice and whose molecular geometries are completely identical except for the arrangement of the ethyl substituent, where

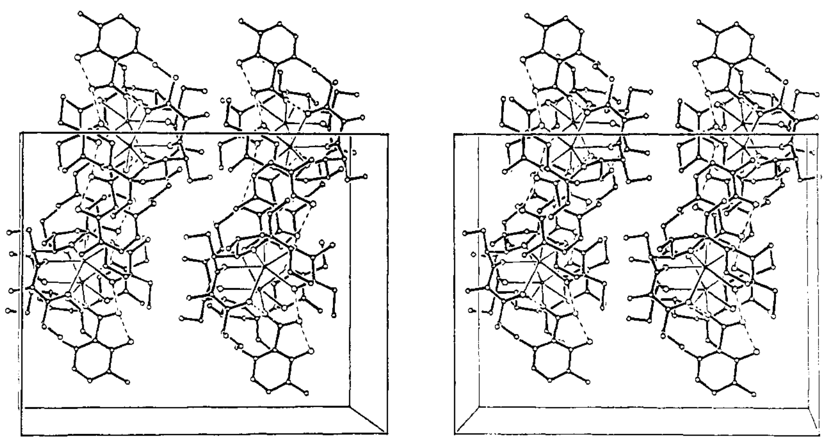

Figure 2. Stereoscopic view of Ag$^+$(lasalocid A$^-$), showing the crystal packing, down the *b* axis with the *a* axis being horizontal and the *c* axis vertical. Broken lines denote hydrogen bonds.

the type A and the type B molecules possess the C25–C26′ (type A[3a]) and the C25–C26 (type B[3a]) ethyl groups, respectively. Therefore, there exist, theoretically, three types of dimers, AA, BB, and AB, which are composed of molecules A and A, B and B, and A and B, respectively, where an exact 2-fold symmetry exists for the first two but not for the last; two ethyl groups in the dimer come close to each other in the dimer AA, go away from each other in the dimer BB, or are directed synchronously in the dimer AB. However, as noted before, the very short C26′···C26′ contact precludes the existence of the dimer AA. Indeed, form I of the Na$^+$(5-Br-L$^-$) salt,[6c] which forms a "head-to-tail" dimer having a pseudo-2-fold symmetry, involves only a BB-type dimer. The Ag$^+$(L$^-$) salt[6d] is an exception: it forms the AA-type "head-to-tail" dimer with a pseudo-2-fold symmetry, where unfavorable C26···C26 contact is, however, avoided by mutual sliding of the pairing molecules toward the phenyl group of the partner molecule to form Ag$^+$–phenyl bondings or vice versa. On the other hand, there seems to be no restriction in the mutual arrangement of the two ethyl groups for the "head-to-head" dimer structure; form II of Na$^+$(5-Br-L$^-$)[6c] and 5-Br-L free acid[4c] both contain the AA-type dimer with a pseudo-2-fold symmetry. Furthermore, occupancy factors for the C26 and C26′ atoms of 0.7 and 0.3 respectively indicate that the BB- and AB-type dimers exist in a 4:6 ratio, respectively, in the present crystal.[17] It is of interest to note here that monomeric lasalocid A–methanol[4a] can be crystallized to give two crystalline forms that contain only the A- and B-type ionophore molecules, respectively, while the present salt consists of the BB- and AB-type dimers in one crystalline form in a disordered manner.

Conclusion

The most novel structural feature of the complex is the existence of an exact 2-fold symmetry in the dimer, and this complex may, therefore, be regarded as a prototype for the 2:2 "head-to-tail" dimeric structure. The salt forms two types of "head-to-tail" dimers, BB and AB, but no AA (defined above), which differ in the mutual arrangement of the C25–C26 ethyl groups; the existence of the AA dimer may be allowed only in the cases in which the 2-fold symmetry in the dimer is significantly broken or the dimer adopts a peculiar structural feature(s), e.g., metal–phenyl bonding in the Ag$^+$(L$^-$) salt.[6d] This suggests that the terminal ethyl group arrangement could play an important role in controlling the "head-to-tail" dimer structure, possibly an essential process in lasalocid A functions, e.g., metal release, since the dimer structure is believed[3] to be a metal-transporting form in membranes (though it is not known whether the dimer with a "head-to-tail" arrangement is an actual form or not). Clearly, further X-ray studies of metal salts involving different circumstances, possibly crystallization from solvents of different polarity, are necessary to understand the whole mechanism of metal ion capture and release by lasalocid A.[3]

Registry No. $Ag^+(C_{34}H_{53}O_8)^-$, 60208-69-7.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table V), atomic coordinates of hydrogen atoms (Table VI), torsion angles (Table VII), and least-squares planes (Table VIII) (3 pages); a listing of structure factors (9 pages). Ordering information is given on any current masthead page.

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(17) It should be noted here that there remains some ambiguity in this ratio value since we cannot rule out some deviation from these site occupations for C26 and C26′, which have not been refined because of a limited number of reflections.

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Preparation and Characterization of Sulfur-Capped Trinuclear Molybdenum(IV) Complexes with Mo_3O_3S Cores and of Sulfur-Bridged Dinuclear Molybdenum(V) Complexes with Mo_2O_3S Cores. Crystal and Molecular Structures of $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ and $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$

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New preparative routes to μ-oxo μ-sulfido cysteinato (**1A**) and edta (**1B**) Mo(V) dimer complexes containing Mo_2O_3S cores are reported, with use of Na_2MoO_4, $N_2H_4\cdot 2HCl$, Na_2S, and L-cysteine hydrochloride (for **1A**) or disodium ethylenediaminetetraacetic acid (for **1B**). Aqua ion, $Mo_2O_3S(aq)^{2+}$ (**1C**), is obtained by the aquation of **1A** in 1 M HCl. The sulfur-capped triangular Mo(IV) aqua ion $Mo_3O_3S(aq)^{4+}$ (**2A**) is obtained from **1C** and $NaBH_4$ in high yield (ca. 70%). The following derivatives of **2A** have been prepared: nitrilotriacetato (Ba^{2+} salt, **2B**; Na^+ salt, **2C**), iminodiacetato (Ca^{2+} salt, **2D**; Na^+ salt, **2E**), L-cysteinato (K^+ salt, **2F**), and thiocyanato (pyH^+ salt, **2G**) complexes. The crystallographic results obtained are as follows: $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2B**), triclinic, $P\bar{1}$, $a = 15.603$ (3) Å, $b = 11.315$ (2) Å, $c = 11.151$ (2) Å, $\alpha = 110.89$ (1)°, $\beta = 95.42$ (1)°, $\gamma = 99.70$ (1)°, $V = 1939.4$ (7) Å^3, $Z = 2$, 4245 unique data ($F_o^2 \geq 3\sigma(F_o^2)$), $R = 3.35\%$; $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (**2F**), triclinic, $P1$, $a = 11.727$ (5) Å, $b = 12.146$ (5) Å, $c = 11.241$ (6) Å, $\alpha = 107.11$ (4)°, $\beta = 118.72$ (4)°, $\gamma = 76.70$ (4)°, $V = 1334.5$ (11) Å^3, $Z = 2$, 4614 unique data ($F_o \geq 6\sigma(F_o)$), $R = 4.12\%$. The cluster anions of **2B′** and **2F′** have approximate symmetries of C_{3v} and C_3, respectively, and contain the same type of incomplete cubane-type core as $Mo_3(\mu\text{-}O)_3(\mu_3\text{-}S)$. The substitution of μ_3-S for μ_3-O causes elongation of Mo–Mo distances by ca. 0.1 Å. As for the electronic spectra of **2A**–**2F** and the relevant complexes with $Mo_3O_{4-n}S_n$ cores, only a slight red shift is observed on substitution of μ_3-S for μ_3-O, while a rather large red shift is observed on the introduction of μ-S. Reduction of **2A** in 1 and 4 M HCl by use of amalgamated zinc gives Mo^{III}_3 species, the oxidation state of which has been determined through titration with Fe^{3+} ion. In 4 M HCl, a mixed oxidation state of $Mo^{IV}Mo^{III}_2$ appears by the addition of Fe^{3+} to Mo^{III}_3. The spectrum of Mo^{III}_3 in 1 M HCl corresponds to that of $Mo^{IV}Mo^{III}_2$ as the HCl concentration increases to 8 M, the former reducing H^+ to give H_2 quantitatively. Cyclic voltammograms of $Mo_3O_3S(aq)^{4+}$ show that the midpoint potential shifts in the positive direction with increasing HCl concentration and that the second reduction peak develops at 8 M HCl. It seems that two- and one-electron processes develop. The cyclic voltammogram of **2D** shows three quasi-reversible waves, whereas that of **2F** shows only one quasi-reversible wave.

Previous investigations in this and other laboratories have demonstrated the preparation, characterization, and structures of a sequence of incomplete cubane-type molybdenum(IV) complexes with Mo_3O_4,[1] Mo_3O_3S,[2] $Mo_3O_2S_2$,[3] Mo_3OS_3,[4] and Mo_3S_4[5]