to that of the peroxymonosulfate ion. The reactions of other peroxy species with $[(NH_3)_5CoS_2O_3]^+$ may also produce the $S_2O_5^{2-}$ species, and their investigation is anticipated.

In summary, HSO_5^- reacts with S-bonded thiosulfate to produce S-coordinated $SOSO_3^{2-}$. This reacts with a further HSO_5^- ion to produce the coordinated metabisulfite complex. In each case, the oxygen addition occurs via a nucleophilic attack of HSO_5^- and transfer of the terminal peroxy oxygen.

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Registry No. HSO_5^-, 12188-01-1; $[(NH_3)_5CoS_2O_3]^+$, 44982-28-7.

Contribution from the Department of Chemistry,
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$[Co(NH_3)_6][LAS]_3$ (LAS = Lasalocid A). A Second-Sphere Complex Involving a Natural Carboxylic Ionophore

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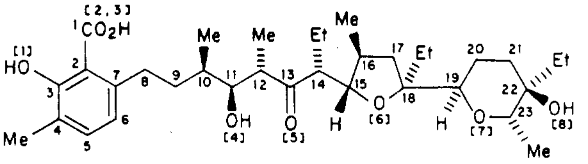
$[Co(NH_3)_6]$[lasalocid A]$_3$ crystallizes in the monoclinic space group $P2_1$ with $a = 12.772$ (3) Å, $b = 29.811$ (7) Å, $c = 16.602$ (3) Å, $\beta = 109.79$ (3)°, and $Z = 2$. Least-squares refinement of the 7115 independent, observed $[I_o \geq 3\sigma(I_o)]$ reflections was carried out to $R = 0.0808$ and $R_w = 0.1064$. Hydrogen atoms, in their idealized positions, were included during refinement. The second-sphere complex consists of a $Co(NH_3)_6^{3+}$ ion surrounded by three lasalocid A anions, each of which is in a cyclic conformation maintained by intraligand hydrogen bonds. The backbone conformation of one of the lasalocid A anions is unusual and has been found in only one previous structure. The complex has approximate 3-fold symmetry. Two water molecules reside within the complex. A network of hydrogen bonds between the $Co(NH_3)_6^{3+}$ ion, the water molecules, and the lasalocid A oxygens maintains the second-sphere coordination. The complex may be regarded as a sphere with hydrophobic groups on the exterior, thus accounting for its solubility in solvents of low polarity.

Lasalocid A (formerly X-537A) (I)[1] is a bacterially produced, carboxylic ionophore capable of serving as a transmembrane mobile carrier for a variety of metal and amine cations.[2-5] The antibiotic activity of lasalocid A is attributed to its ability to perturb transmembrane ion gradients, thereby interfering with natural transport systems for ions such as H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}. Lasalocid A has proven useful as a laboratory tool for transport studies involving both natural and artificial membranes, and it has been exploited commercially as a feed additive in the poultry industry because of its anticoccidial activity.[5] Furthermore, it has been shown that lasalocid A has pronounced cardiovascular effects.[5]



I

The current mechanistic view of lasalocid-mediated cation transport involves formation within the membrane of a hydrophobic lasalocid–cation complex in which the lasalocid A anion (hereafter abbreviated LAS) surrounds the cation with its polar groups, leaving a hydrophobic exterior.[4,5] This model is supported by a number of X-ray crystallographic studies of LAS complexes of mono- and divalent metal cations.[6] Because of the relatively small size of lasalocid A, dimeric (2:2 cation:anion) structures are usually found for complexes of the monovalent cations Na^+ and Ag^+ in order to provide a sufficiently large hydrophobic "shell" about the cation. A 1:2 complex is formed with Ba^{2+}, and the Cs^+ complex is polymeric.[6] In all these structures the LAS ligand adopts a cyclic conformation maintained by intramolecular hydrogen bonding. The five oxygens, O_4, O_5, O_6, O_7, and O_8, are involved in cation binding in nearly all these structures, but the carboxylate group is not always directly bound to the cation, and binding by the phenolic oxygen is rare. A crystallographic study of the 1:1 complex of LAS with the cation of the amine (*R*)-(+)-1-amino-1-(4-bromophenyl)ethane revealed hydrogen bonds from the $-NH_3^+$ group to O_2, O_6, and O_8 of LAS, which was found in the usual cyclic conformation.[7]

Structures of LAS complexes in the solution phase are not as well established, but there is considerable evidence that these differ from the solid-state structures.[8] NMR studies in this laboratory have shown that the LAS oxygens used for binding to divalent and trivalent cations depend upon both the charge of the cation and the polarity of the solvent, and in some cases fluxional behavior is observed.[8,9] Also, the Na^+ complex, which is dimeric in the solid state and in solutions of nonpolar solvents, becomes monomeric in polar solvents.[10]

Colquhoun and co-workers have shown that crown ether ionophores such as 18-crown-6 and its analogues form M–N–H···O hydrogen-bonded adducts with transition-metal–amine complexes.[11] These observations, combined with the fact that LAS forms adducts with a variety of organic amine cations,[2-5,7,12,13]

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prompted our investigation of the interaction of Werner-type ammine complexes with LAS. We previously prepared the following complexes and characterized them by elemental analyses, molecular weight data, and UV-visible, CD, and ^{13}C NMR spectroscopy:[14] $[Co(NH_3)_5Cl][LAS]_2$, $[Co(NH_3)_6][LAS]_3$, $[Cr(NH_3)_6][LAS]_3$, Δ-$[Co(en)_3][LAS]_3$, Λ-$[Co(en)_3][LAS]_3$, and $[Pt(NH_3)_6][LAS]_4$. These complexes are readily soluble in solvents of low polarity such as chloroform. It was proposed that these "second-sphere" complexes are maintained through M–N–H···O hydrogen bonds, but it was not clear whether all the LAS anions could serve as multidentate ligands having the usual cyclic conformation, especially when three or four such ligands interact with a single ammine–metal cation.

We recently succeeded in obtaining crystals of $[Co(NH_3)_6]$-$[LAS]_3$ suitable for X-ray work, and herein we report the results of a crystal structure determination of this second-sphere complex that contains 133 non-hydrogen atoms.

Experimental Section

$[Co(NH_3)_6][LAS]_3$ was prepared as described previously[14] and obtained as a microcrystalline powder. Crystals used for crystallography were grown by vapor diffusion of acetonitrile into a dilute solution of the complex in ethyl acetate over a period of 1–2 weeks.

Collection and Reduction of the X-ray Data. An orange-yellow, monoclinic crystal of approximate dimensions 0.5 × 0.3 × 0.3 mm was attached to the end of a glass fiber with epoxy cement. This was mounted on a Syntex $P2_1$ diffractometer, and standard Syntex programs were used to obtain unit cell dimensions and the orientation matrix by least-squares refinement of 2θ, ω, and χ from 15 centered reflections. Data were collected by the θ–2θ scan technique at 25 ± 2 °C. Two monitor reflections (080 and $30\bar{3}$), measured after every 100 reflections, showed some variation in intensity with an overall decrease of 10% in each case during the data collection. Decay corrections were made by using observed intensities of these monitor reflections. A total of 12783 reflections were collected. Intensities and standard deviations were calculated by using $I = r(S - RB)$ and $\sigma^2(I) = r^2(S + R^2B)$, where r is the scan rate in deg/min, S is the total scan count, R is the scan to background time ratio, and B is the background count. Intensities were corrected for absorption and for Lorentz–polarization effects and averaged for symmetry-related reflections. A total of 7115 reflections from a total of 7999 independent reflections have $I_o \geq 3\sigma(I_o)$ and are considered to be observed. These data were used in the subsequent structure determination and refinement.

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis revealed the position of the cobalt atom. The electron density map computed from the observed structure factors with phase angles from the Co atom showed perfect pseudomirror symmetry; i.e., the phase angles are either 0 or π, and the pair peaks are seen at (x, y, z) and (x, $-y$, z). One additional peak found in this electron density map was introduced into the subsequent structure factor calculation. The second electron density map also showed nearly perfect pseudomirror symmetry, but a few peak pairs showed slightly different peak heights. A simple pseudosymmetry checking program was written in order to find out which peak pair had the most significant effect on the peak heights. The peak with the largest $|P+ - P-|/|P+ + P-|$ was introduced into the next structure factor calculation, and then the third electron density map was calculated with the new phase angles. The above procedure was repeated 31 times. The 34th electron density map showed 112 significant peaks. A least-squares refinement indicated that 15 peaks with very large thermal parameters were false peaks. The electron density map computed with the observed structure factors with phase angles from the remaining 97 atoms showed the positions of all non-hydrogen atoms except for the partially occupied water molecules, W(3), W(4), W(5), and W(6).

After four cycles of block-diagonal, least-squares refinement in which all atoms were varied isotropically, a difference electron density map was computed. This revealed four additional peaks with significant electron density (~2 e/Å^3), but none of them were located within range of hydrogen bonding with the complex. The peaks were assigned as partially occupied water oxygens and were introduced into subsequent refinement. Coordinates of all hydrogen atoms were calculated by using idealized geometry, and their thermal parameters were varied isotropically during least-squares refinement. Idealized geometries for the ammine groups were taken from a neutron diffraction study[15] of $[H_3N$–$(CH_2)_4$–$NH_3][H_2PO_4]_2$ (N–H is 1.041 Å, C–N–H is 111.7°, and H–N–H is 107.2°), and these groups were oriented so as minimize the N···O(LAS) distances. All non-hydrogen atoms except for the partially occupied water oxygens were refined anisotropically with block-matrix least-squares techniques. The isotropic thermal parameters of the partially occupied water oxygens were fixed at 6.0 Å^2 in the early cycles, and the positional and occupancy parameters were varied in the block-matrix, least-squares refinement. During refinement, a four-block matrix was used in which the first block contained the scale parameter along with parameters for the $Co(NH_3)_6$ cation and the six water molecules. Blocks 2–4 contained all parameters for LAS ligands A, B, and C, respectively. After three cycles of refinement, the hydrogen positions were recalculated. This was repeated three times for a total of nine cycles of least-squares refinement. After a final cycle, using improved coordinates for ammine hydrogens (vide infra), $R = 0.0808$ and $R_w = 0.1064$. During refinement, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The maximum Δ/σ for positional parameters in the final cycle of refinement was 0.084, and the highest peak found in the final difference map was 0.18 e/Å^3 (near the Co atom). Atomic scattering factors were taken from ref 16.

In order to explore more fully the pattern of hydrogen bonding between the ammine groups and the LAS ligands, a program was written to compute hydrogen-bond energies as the amine groups are rotated about the Co–N bond in the potential field of neighboring oxygen atoms. The semiempirical potential function developed by Vedani[17] was used in these calculations with the idealized ammine geometry described above. Distinct energy minima were found for each of the six ammine groups. Differences found between maximum and minimum energy conformations are as follows (in kcal/mol): $N(1)H_3$, 7.47; $N(2)H_3$, 2.26; $N(3)H_3$, 4.06; $N(4)H_3$, 3.05; $N(5)H_3$, 5.24; $N(6)H_3$, 1.97. Hydrogen atom coordinates for the conformations of minimum energy are very nearly the same as those used during least-squares refinement. A final cycle of least-squares refinement was carried out by using the ammine hydrogen coordinates determined by energy minimization. Thermal parameters for ammine hydrogens were allowed to vary in the final least-squares refinement. Although these parameters are relatively large (B = 14–32 Å^2), they converged during refinement (maximum $\Delta/\sigma = 0.74$).

A test for the absolute configurations of chiral centers on the LAS ligands was carried out by using 11935 nonaveraged reflections and anomalous scattering factors for cobalt. After three cycles of refinement each in a positive (+) coordinate system and in the enantiomeric negative (−) coordinate system, weighted R values were $R_w(+) = 0.1023$ and $R_w(-) = 0.1027$. Although the difference between these R values is small, the R factor ratio of 1.004 indicates a 99.5% probability[18] that the configurations reported in this paper are correct. All computations were carried out on a VAX 8600 computer at the University of Kansas using programs written by F.T.

Results and Discussion

The $[Co(NH_3)_6][LAS]_3$ complex has *approximate* 3-fold symmetry as may be seen from the stereoview in Figure 1. The $[Co(NH_3)_6]^{3+}$ ion has very nearly O_h symmetry, with Co–N bond lengths ranging from 1.943 (8) to 1.969 (7) Å and N–Co–N angles ranging from 87.9 (4) to 92.0 (4)°. In comparison, the average Co–N distance found[19] in $[Co(NH_3)_6]Cl_3$ is 1.963 Å, and the maximum deviation of the N–Co–N angle from ideality is 2.1°.

In the present complex, the cation is surrounded by three LAS anions (labeled A, B, and C), each of which has a cyclic conformation as observed in other structures of lasalocid A complexes. A network of hydrogen bonds connects the ammine groups to various LAS oxygens and to two molecules of water, W(1) and W(2), which lie within the "cage" of LAS anions. These are shown in Figure 1 and summarized in Table III. These hydrogen bonds were not found in the difference electron density maps; the coordinates of hydrogen atoms comprising these bonds were determined in the following manner. The O–H···O bonds (intraligand and water–ligand) are assumed to occur at the shortest O···O distances, and an O–H distance of 1.0 Å was used. The H–O–H angle for W(1) and W(2) was assumed to be 111.6°. The orientation of each $-NH_3$ group was determined by a computational procedure (see Experimental Section) in which a

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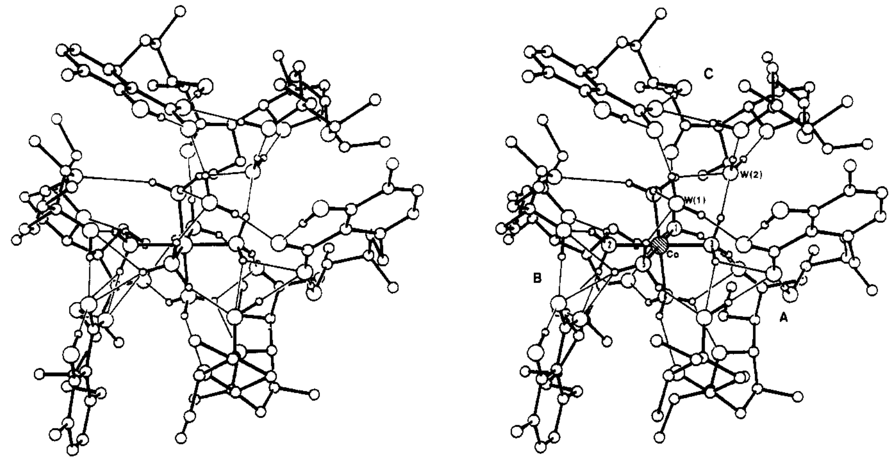

Figure 1. Stereoview showing the overall structure of the $[Co(NH_3)_6][LAS]_3$ complex and the hydrogen-bonding network including two water molecules, W(1) and W(2). The ammine nitrogens are numbered, and LAS ligands are labeled A, B, and C.

Table I. Summary of Crystallographic Data for the Second-Sphere Complex of $[Co(NH_3)_6]^{3+}$ and Lasalocid A

formula	$[Co(NH_3)_6][C_{34}H_{53}O_8]_3{\cdot}3.3H_2O$
cryst syst	monoclinic
space group	$P2_1$
a, Å	12.772 (3)
b, Å	29.811 (7)
c, Å	16.602 (3)
β, deg	109.79 (3)
V, Å^3	5948 (2)
T, °C	25 ± 2
Z	2
d_{calcd}, g/cm^3	1.111
cryst dimens, mm	0.5 × 0.3 × 0.3
radiatn[a]	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)
abs coeff (μ), cm^{-1}	2.2278
scan rate, deg/min	1.0–20.0 (θ–2θ)
scan range, deg	1.2° below Kα to 1.2° above Kα
bkgd/scan time ratio	1/3
std reflcns	$30\bar{3}$, 080
total reflcns collcd	12783[b]
R_{sym}	0.078
no. of independent reflcns	7999
no. of obsd reflcns [$I_o \geq 3\sigma(I_o)$]	7115
no. of variables	1413
R	0.0808
R_w	0.1064

[a] Graphite-monochromated radiation. [b] Two octants with $2\theta < 45°$, hkl and $hk\bar{l}$, and two octants with $2\theta < 30°$, $h\bar{k}\bar{l}$ and $h\bar{k}l$.

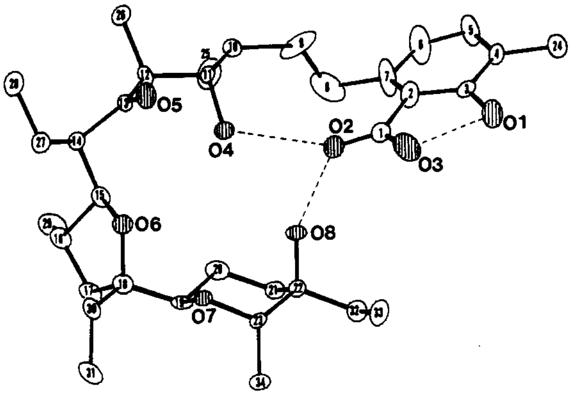

Figure 2. ORTEP drawing of LAS ligand A. Dashed lines indicate locations of intraligand hydrogen bonds.

minimum Coulombic potential was found as the Co–N bond is rotated. By this procedure, the most probable positions of ammine protons were located, and the pattern of Co–N–H···O hydrogen bonds was determined. On the basis of these results, the hydrogen-bonding scheme described in Figure 1 and Table III is proposed. Three bifurcated and one trifurcated hydrogen bonds involving ammine groups are proposed.

Colquhoun et al.[11] have found that, for hydrogen bonds between metal ammine complexes and crown ether oxygens, the N···O distances are often unusually long (3.0–3.4 Å). The N(4)–H3(N4)···O(7B) bond, for which the N···O distance is 3.758 Å, is the only one outside this range in Table III. The existence of this (weak) hydrogen bond is proposed here because of the favorable juxtaposition of H3(N4) and O(7B) and the fact that no other oxygen is in a favorable position for interaction. With idealized geometry used for the ammine group (see Experimental Section), the H···O distance for this bond is 2.771 Å. A hydrogen bond of similar length (2.746 Å) was found in a neutron diffraction study of methyl β-D-galactopyranoside.[20] The N(4) ammine differs from the others in that it forms only this one, very weak interaction with the LAS ligands; the other hydrogen bonds from N(4) are to W(1) and W(2). The other ammines differ widely in their pattern of interactions with the LAS ligands. For example, $N(1)H_3$ is hydrogen bonded to the C(13) carbonyl oxygen of all three ligands, whereas $N(2)H_3$ interacts only with ligand B.

The two water molecules within the complex are each involved in four hydrogen bonds. Each donates two hydrogens to form bonds to LAS oxygens, and each accepts hydrogens from two different ammine groups. These bonds are identified in Table III. Water molecules are involved in the hydrogen-bonding network in many of the reported structures of LAS complexes.[6] Eight other water molecules, each with occupancy ~$^1/_3$, are found in the unit cell, but these are not closely associated with the complex.

The three LAS ligands A, B, and C differ markedly in the manner by which they are attached to the $Co(NH_3)_6{}^{3+}$ ion. Ligands A and B interact via hydrogen bonds with four and five different ammine groups, respectively, and A is bound also to W(1). On the other hand, probably for steric reasons, ligand C bonds only to $N(1)H_3$ and W(1) and W(2), which are, in turn, bound to $N(4)H_3$ and $N(5)H_3$ and $N(3)H_3$ and $N(4)H_3$, respectively. Thus ligand C is held in place largely by "third-sphere" coordination to the Co(III) ion. Similar third-sphere coordination very likely occurs in the analogous Pt(IV)–ammine complex in which *four* LAS anions are bound.[14]

Three intraligand hydrogen bonds are found for each LAS anion (see Table III and Figures 2–4). The pattern of these bonds is the same for anions A and C, but anion B differs in that O(8) forms a hydrogen bond to O(3) rather than to O(2). This may result from the fact that, in anions A and C, O(3) is involved in hydrogen bonding to W(1) and, in B, O(2) is bound to both $N(2)H_3$ and $N(5)H_3$. Both these patterns of intraligand hydrogen bonding have been observed in the other structures of LAS complexes, and the O–O distances observed here are within the ranges

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Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Co	0.29581 (8)	0.00000 (5)	0.65180 (6)	2.93
N(1)	0.4550 (5)	−0.0150 (3)	0.6921 (4)	3.78
N(2)	0.3326 (6)	0.0633 (3)	0.6519 (5)	4.13
N(3)	0.2553 (6)	−0.0629 (3)	0.6536 (5)	3.98
N(4)	0.3016 (6)	0.0073 (3)	0.7702 (4)	4.78
N(5)	0.1375 (6)	0.0164 (3)	0.6098 (5)	4.27
N(6)	0.2893 (6)	−0.0073 (3)	0.5323 (4)	4.49
W(1)	0.0683 (8)	−0.0239 (4)	0.7437 (6)	7.92
W(2)	0.3797 (6)	−0.0842 (3)	0.8210 (5)	6.37
W(3)	0.059 (2)	−0.222 (1)	0.233 (2)	6.95[b]
W(4)	0.032 (2)	−0.222 (1)	0.360 (2)	8.11[b]
W(5)	0.770 (3)	−0.256 (1)	0.522 (2)	8.35[b]
W(6)	0.660 (3)	−0.183 (1)	0.269 (2)	9.16[b]
C(1A)	0.0133 (8)	−0.1362 (4)	0.6390 (7)	4.94
C(2A)	−0.0005 (9)	−0.1778 (4)	0.6845 (9)	5.70
C(3A)	−0.0805 (7)	−0.1775 (4)	0.7257 (6)	4.20
C(4A)	−0.0991 (7)	−0.2167 (4)	0.7695 (6)	4.35
C(5A)	−0.044 (1)	−0.2538 (5)	0.766 (1)	8.32
C(6A)	0.018 (2)	−0.2556 (7)	0.717 (2)	14.26
C(7A)	0.043 (2)	−0.2205 (5)	0.674 (2)	12.92
C(8A)	0.117 (2)	−0.2313 (6)	0.616 (1)	10.91
C(9A)	0.221 (1)	−0.2221 (8)	0.672 (2)	17.16
C(10A)	0.3181 (9)	−0.2268 (4)	0.6257 (7)	5.03
C(11A)	0.3434 (7)	−0.1782 (3)	0.6047 (5)	3.86
C(12A)	0.4399 (8)	−0.1746 (4)	0.5715 (6)	4.59
C(13A)	0.4573 (7)	−0.1261 (3)	0.5512 (5)	3.63
C(14A)	0.4864 (8)	−0.1176 (3)	0.4716 (6)	4.12
C(15A)	0.3725 (8)	−0.1160 (3)	0.3978 (6)	4.39
C(16A)	0.376 (1)	−0.1217 (4)	0.3067 (6)	5.73
C(17A)	0.267 (1)	−0.1008 (4)	0.2544 (6)	5.14
C(18A)	0.2444 (9)	−0.0630 (4)	0.3110 (6)	5.03
C(19A)	0.1276 (8)	−0.0638 (4)	0.3137 (5)	4.37
C(20A)	0.0961 (9)	−0.1044 (3)	0.3541 (6)	4.59
C(21A)	−0.0181 (8)	−0.0993 (4)	0.3589 (6)	4.32
C(22A)	−0.0300 (7)	−0.0560 (3)	0.4039 (5)	3.83
C(23A)	0.0059 (6)	−0.0159 (3)	0.3608 (5)	3.50
C(24A)	−0.182 (1)	−0.2138 (6)	0.818 (1)	7.53
C(25A)	0.303 (1)	−0.2591 (5)	0.550 (1)	8.65
C(26A)	0.5530 (9)	−0.1910 (4)	0.6422 (8)	5.62
C(27A)	0.5587 (8)	−0.0771 (4)	0.4783 (7)	5.07
C(28A)	0.676 (1)	−0.0869 (6)	0.5479 (9)	7.39
C(29A)	0.382 (2)	−0.1725 (6)	0.2873 (8)	8.18
C(30A)	0.2803 (9)	−0.0178 (4)	0.2863 (7)	5.15
C(31A)	0.203 (1)	−0.0006 (5)	0.1977 (7)	6.60
C(32A)	−0.1497 (9)	−0.0497 (4)	0.4065 (6)	5.40
C(33A)	−0.1671 (9)	−0.0056 (5)	0.4479 (9)	6.61
C(34A)	−0.0740 (8)	−0.0042 (4)	0.2739 (6)	5.01
O(1A)	−0.1379 (8)	−0.1406 (3)	0.7266 (7)	7.76
O(2A)	0.0670 (6)	−0.1371 (3)	0.5900 (6)	6.38
O(3A)	−0.0315 (9)	−0.1015 (3)	0.6544 (6)	7.46
O(4A)	0.2504 (5)	−0.1587 (3)	0.5394 (4)	5.03
O(5A)	0.4487 (6)	−0.0960 (3)	0.5956 (5)	5.36
O(6A)	0.3216 (5)	−0.0732 (2)	0.3972 (4)	4.61
O(7A)	0.1185 (5)	−0.0239 (2)	0.3602 (3)	3.52
O(8A)	0.0469 (5)	−0.0570 (2)	0.4909 (3)	3.89
C(1B)	0.0510 (8)	0.1070 (4)	0.4658 (5)	4.25
C(2B)	−0.0205 (8)	0.1151 (3)	0.3738 (5)	3.92
C(3B)	−0.1317 (7)	0.1271 (3)	0.3593 (5)	3.97
C(4B)	−0.2068 (7)	0.1340 (3)	0.2721 (6)	4.22
C(5B)	−0.1644 (8)	0.1292 (4)	0.2077 (5)	4.70
C(6B)	−0.0551 (8)	0.1183 (4)	0.2204 (6)	4.98
C(7B)	0.0179 (7)	0.1099 (3)	0.3044 (5)	3.91
C(8B)	0.1384 (8)	0.0980 (4)	0.3131 (6)	4.58
C(9B)	0.2073 (8)	0.1386 (3)	0.3248 (6)	4.46
C(10B)	0.3333 (9)	0.1309 (4)	0.3444 (7)	5.28
C(11B)	0.3814 (8)	0.1045 (4)	0.4344 (6)	4.28
C(12B)	0.5102 (7)	0.1014 (3)	0.4679 (6)	4.23
C(13B)	0.5472 (7)	0.0800 (4)	0.5534 (7)	4.45
C(14B)	0.6405 (7)	0.1026 (3)	0.6282 (6)	4.29
C(15B)	0.5845 (7)	0.1413 (4)	0.6629 (6)	4.26
C(16B)	0.6642 (8)	0.1736 (4)	0.7169 (7)	4.83
C(17B)	0.5979 (9)	0.1950 (4)	0.7690 (8)	5.71
C(18B)	0.5321 (7)	0.1523 (4)	0.7880 (6)	4.33
C(19B)	0.4133 (7)	0.1666 (3)	0.7782 (5)	3.88
C(20B)	0.3358 (7)	0.1791 (3)	0.6896 (5)	3.92
C(21B)	0.2171 (9)	0.1887 (4)	0.6885 (7)	4.97
C(22B)	0.1727 (7)	0.1512 (3)	0.7324 (5)	3.82
C(23B)	0.2594 (7)	0.1404 (3)	0.8192 (5)	3.80
C(24B)	−0.3234 (8)	0.1472 (5)	0.2573 (7)	5.68
C(25B)	0.392 (1)	0.1746 (5)	0.3432 (9)	6.69
C(26B)	0.5562 (9)	0.0749 (5)	0.4117 (7)	6.22
C(27B)	0.7091 (8)	0.0699 (4)	0.6924 (7)	5.02
C(28B)	0.780 (1)	0.0405 (6)	0.656 (1)	7.65
C(29B)	0.702 (1)	0.2085 (5)	0.665 (1)	7.31
C(30B)	0.5938 (8)	0.1295 (4)	0.8678 (6)	5.18
C(31B)	0.6001 (9)	0.1544 (5)	0.9537 (7)	6.73
C(32B)	0.0619 (9)	0.1650 (5)	0.7363 (7)	5.80
C(33B)	0.007 (1)	0.1316 (5)	0.777 (1)	7.04
C(34B)	0.2689 (9)	0.1765 (4)	0.8866 (6)	5.34
O(1B)	−0.1764 (6)	0.1309 (3)	0.4196 (4)	5.74
O(2B)	0.1477 (6)	0.0930 (3)	0.4825 (4)	5.47
O(3B)	0.0091 (6)	0.1123 (4)	0.5221 (4)	7.18
O(4B)	0.3530 (5)	0.1271 (3)	0.4995 (4)	5.49
O(5B)	0.5063 (5)	0.0446 (2)	0.5653 (4)	4.30
O(6B)	0.5294 (5)	0.1207 (2)	0.7188 (4)	4.13
O(7B)	0.3643 (5)	0.1301 (2)	0.8103 (4)	3.99
O(8B)	0.1619 (5)	0.1110 (2)	0.6845 (4)	4.09
C(1C)	0.171 (1)	0.0209 (6)	0.9491 (7)	7.18
C(2C)	0.1606 (9)	0.0650 (4)	0.9919 (6)	4.69
C(3C)	0.0539 (8)	0.0792 (5)	0.9819 (7)	5.47
C(4C)	0.0350 (8)	0.1190 (5)	1.0175 (6)	5.17
C(5C)	0.123 (1)	0.1437 (4)	1.0659 (7)	5.35
C(6C)	0.2339 (8)	0.1296 (5)	1.0767 (7)	5.89
C(7C)	0.2519 (7)	0.0915 (4)	1.0380 (6)	4.06
C(8C)	0.3715 (9)	0.0822 (4)	1.0437 (8)	5.84
C(9C)	0.4287 (8)	0.0481 (4)	1.1146 (6)	4.64
C(10C)	0.5476 (8)	0.0346 (4)	1.1172 (7)	5.02
C(11C)	0.5423 (7)	0.0135 (4)	1.0340 (6)	4.33
C(12C)	0.6563 (7)	−0.0035 (4)	1.0301 (6)	4.33
C(13C)	0.6382 (8)	−0.0251 (4)	0.9435 (6)	4.18
C(14C)	0.7058 (8)	−0.0668 (4)	0.9457 (6)	4.44
C(15C)	0.6603 (9)	−0.1050 (4)	0.9884 (6)	5.13
C(16C)	0.740 (1)	−0.1435 (5)	1.0293 (8)	6.76
C(17C)	0.662 (1)	−0.1805 (5)	1.0335 (8)	7.11
C(18C)	0.5539 (8)	−0.1731 (4)	0.9582 (6)	5.10
C(19C)	0.450 (1)	−0.1709 (5)	0.9831 (8)	6.61
C(20C)	0.442 (1)	−0.1330 (6)	1.0370 (8)	7.79
C(21C)	0.324 (2)	−0.1317 (8)	1.049 (1)	11.12
C(22C)	0.227 (2)	−0.1330 (6)	0.961 (1)	9.74
C(23C)	0.249 (1)	−0.1732 (6)	0.916 (2)	10.53
C(24C)	−0.086 (1)	0.1355 (5)	1.0000 (8)	6.67
C(25C)	0.599 (1)	0.0050 (8)	1.1947 (7)	8.66
C(26C)	0.7399 (8)	0.0344 (5)	1.0390 (8)	6.13
C(27C)	0.7092 (9)	−0.0798 (5)	0.8577 (7)	5.79
C(28C)	0.777 (1)	−0.0470 (5)	0.8290 (9)	7.06
C(29C)	0.828 (1)	−0.1281 (6)	1.116 (1)	9.90
C(30C)	0.5451 (9)	−0.2032 (4)	0.8853 (7)	5.15
C(31C)	0.523 (1)	−0.2522 (5)	0.896 (1)	7.80
C(32C)	0.090 (3)	−0.136 (1)	0.955 (2)	16.75
C(33C)	0.065 (3)	−0.099 (1)	0.992 (2)	15.05
C(34C)	0.246 (3)	−0.219 (1)	0.973 (4)	21.40
O(1C)	−0.0401 (7)	0.0569 (4)	0.9362 (6)	7.97
O(2C)	0.256 (1)	0.0047 (5)	0.9575 (8)	12.12
O(3C)	0.075 (1)	0.0016 (5)	0.9025 (9)	10.37
O(4C)	0.4738 (6)	−0.0256 (3)	1.0178 (5)	5.90
O(5C)	0.5768 (6)	−0.0083 (3)	0.8773 (4)	5.49
O(6C)	0.5685 (5)	−0.1276 (3)	0.9263 (4)	4.77
O(7C)	0.3570 (6)	−0.1720 (3)	0.9061 (5)	5.99
O(8C)	0.2338 (8)	−0.0957 (3)	0.9115 (6)	7.36

[a] The thermal parameters are of the form $B_{eq} = {}^{8}/_{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$. [b] Occupancy parameters of W(3), W(4), W(5), and W(6) are 0.30 (1), 0.36 (1), 0.30 (1), and 0.34 (1), respectively. These partially occupied water molecules are refined with isotropic thermal parameters.

of those reported earlier.[6] The O(2)–O(4) and O(8)–O(2) or O(8)–O(3) hydrogen bonds maintain the cyclic conformation of the anions.

The overall conformations of the carbon backbone for ligands B and C differ only slightly, as may be seen by comparing Figures 3 and 4 and the torsion angles given in Table IV. Ligand A,

Table III. Dimensions of Hydrogen Bonds

X-H···O	H···O, Å	X---O, Å	∠X-H···O, deg	*E*, kcal/mol	
N(1)-H1(N1)···O(5B)	2.052	2.994 (11)	148.9	1.9844	
N(1)-H(2)(N1)···O(5A)	1.915	2.881 (11)	153.3	2.7678	
N(1)-H3(N1)···O(5C)	1.914	2.945 (9)	170.8	3.3802	
N(2)-H1(N2)···O(6B)	2.051	2.931 (10)	140.6	1.6202	
N(2)-H(2)(N2)···O(8B)	1.843	2.805 (11)	151.9	2.5988	
N(2)-H3(N2)···O(2B)	2.318	3.126 (9)	133.4	0.5728	} bifurcated
N(2)-H3(N2)···O(4B)	2.318	3.247 (11)	147.8	0.8698	
N(3)-H1(N3)···O(5A)	2.144	3.100 (13)	151.9	1.6315	
N(3)-H2(N3)···O(8A)	2.181	3.089 (8)	144.5	1.2427	} bifurcated
N(3)-H2(N3)···O(2A)	2.406	3.176 (11)	129.8	0.3739	
N(3)-H3(N3)···W(2)	1.894	2.769 (10)	139.4	2.0147	
N(4)-H1(N4)···W(2)	2.016	2.931 (13)	144.8	1.9675	
N(4)-H2(N4)···W(1)	2.064	3.009 (13)	149.7	1.9567	
N(4)-H3(N4)···O(7B)	2.771	3.758 (12)	158.4	0.2421	
N(5)-H1(N5)···O(2B)	2.303	3.142 (12)	136.7	0.6767	} trifurcated
N(5)-H1(N5)···O(3B)	2.416	3.369 (13)	151.8	0.6859	
N(5)-H1(N5)···O(8B)	2.336	3.051 (11)	124.8	0.3743	
N(5)-H2(N5)···W(1)	1.953	2.916 (14)	152.3	2.6046	
N(5)-H3(N5)···O(8A)	1.930	2.911 (10)	156.3	2.8680	
N(6)-H1(N6)···O(5A)	2.444	3.288 (10)	137.3	0.4354	} bifurcated
N(6)-H1(N6)···O(6A)	2.322	3.114 (11)	131.7	0.5308	
N(6)-H2(N6)···O(5B)	2.158	3.057 (10)	143.4	1.2950	
N(6)-H3(N6)···O(7A)	2.172	2.992 (8)	134.1	0.9328	
W(1)-H1(W1)···O(3A)	1.823	2.810 (13)	168.1		
W(1)-H2(W1)···O(3C)	1.734	2.718 (18)	167.9		
W(2)-H1(W2)···O(6C)	1.780	2.773 (9)	172.2		
W(2)-H2(W2)···O(8C)	1.787	2.782 (15)	172.2		
O(1A)-H(O1A)···O(3A)	1.397	2.397 (17)	180.0		
O(4A)-H(O4A)···O(2A)	1.819	2.819 (12)	180.0		
O(8A)-H(O8A)···O(2A)	1.865	2.865 (11)	180.0		
O(1B)-H(O1B)···O(3B)	1.467	2.467 (9)	180.0		
O(4B)-H(O4B)···O(2B)	1.737	2.737 (10)	180.0		
O(8B)-H(O8B)···O(3B)	1.742	2.742 (8)	180.0		
O(1C)-H(O1C)···O(3C)	1.396	2.396 (19)	180.0		
O(4C)-H(O4C)···O(2C)	1.770	2.770 (15)	180.0		
O(8C)-H(O8C)···O(2C)	2.075	3.075 (18)	180.0		

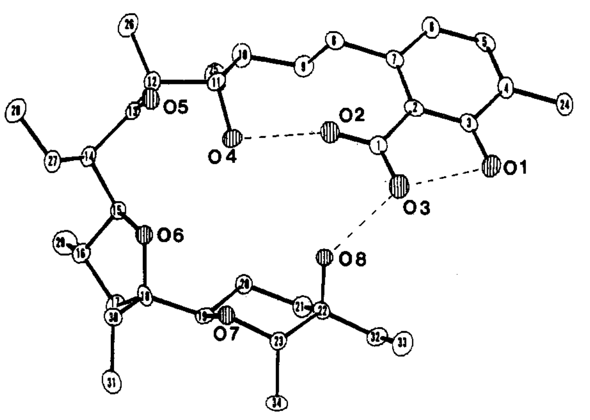

Figure 3. ORTEP drawing of LAS ligand B. Dashed lines indicate locations of intraligand hydrogen bonds.

however, differs significantly from B and C in that torsion angles in the C(2)–C(11) region are of opposite sign, i.e. the carbon backbone in A bends at C(8) toward the opposite side of the phenyl ring. The difference is that of a "crank motion". The conformation of A has been found for only one other LAS anion, that of *one* of the 5-nitro–LAS ligands in the dimeric Ag^+ complex.[6] Other conformational differences among the three ligands are minor with the exception of the ethyl moiety at C(22). The orientation of the ethyl group differs markedly for ligand C (compare Figures 2–4), but both these orientations have been found in other structures.[6] The six-membered oxygen-containing rings are in their usual[6] chair conformations.

Thus, although the overall shapes of the three LAS ligands are generally similar, no two have the same combination of backbone conformation and intraligand oxygen bonding. Because of the extreme flexibility of the LAS ion, a wide range of conformations is possible, and the observed structure represents the outcome of a competition between LAS–cation attractions, intraligand at-

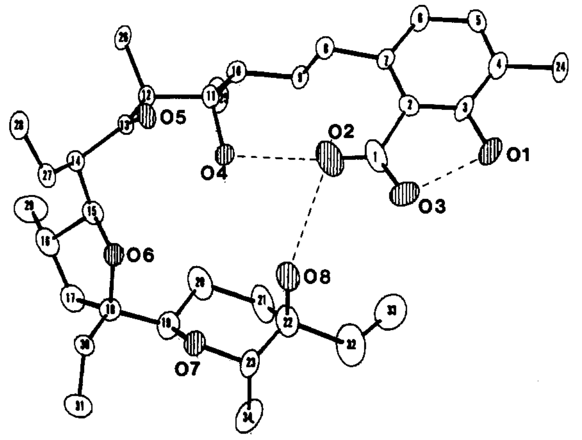

Figure 4. ORTEP drawing of LAS ligand C. Dashed lines indicate locations of intraligand hydrogen bonds.

Table IV. Ligand Backbone Torsion Angles (deg)

	ligand A	ligand B	ligand C
C(2)–C(7)–C(8)–C(9)	87 (2)	–87 (1)	–85 (1)
C(7)–C(8)–C(9)–C(10)	–176 (1)	173.5 (8)	174.9 (9)
C(8)–C(9)–C(10)–C(11)	101 (2)	–63 (1)	–60 (1)
C(9)–C(10)–C(11)–C(12)	173 (1)	–170.8 (8)	–177.5 (9)
C(10)–C(11)–C(12)–C(13)	179.0 (7)	175.7 (9)	178.5 (9)
C(11)–C(12)–C(13)–C(14)	–140.4 (7)	–130.6 (7)	–140.6 (8)
C(12)–C(13)–C(14)–C(15)	84.6 (8)	80.0 (8)	70.0 (9)
C(13)–C(14)–C(15)–C(16)	–162.6 (9)	–164.0 (8)	–156.5 (9)
C(14)–C(15)–C(16)–C(17)	–158.4 (9)	–158.4 (8)	–159.7 (9)
C(15)–C(16)–C(17)–C(18)	32 (1)	39 (1)	30 (1)
C(16)–C(17)–C(18)–C(19)	–132.7 (9)	–139.5 (8)	–126 (1)
C(17)–C(18)–C(19)–C(20)	64 (1)	67 (1)	65 (2)
C(18)–C(19)–C(20)–C(21)	175.5 (8)	174.9 (8)	173 (1)
C(19)–C(20)–C(21)–C(22)	–54 (1)	–50 (1)	–53 (2)
C(20)–C(21)–C(22)–C(23)	53.5 (9)	49 (1)	54 (2)

tractions, and interligand steric repulsions. If this structure occurs also in solutions of low-polarity solvents, it accounts for the solubility of the complex in such solvents and indicates that LAS might effect membrane transport of transition-metal–ammine complexes.

It is of interest to compare this structure with that of the 1:1 complex of LAS with the cation of (*R*)-(+)-1-amino-1-(4-bromophenyl)ethane.[7] In the 1:1 complex, hydrogen bonds from the $-NH_3^+$ group to O(2), O(6), and O(8) (using the numbering scheme shown in I) were found with N···O distances ranging from 2.80 to 2.90 Å. A similar pattern of hydrogen bonding is observed in the present structure between N(2)H$_3$ and ligand B, except for the bifurcation of the bond from N(2)H(3) (Table III). Ligand B also bonds to N(1)H$_3$, N(4)H$_3$ (long bond), N(5)H$_3$, and N(6)H$_3$. In the 1:1 complex LAS has the usual cyclic conformation, and the pattern of intraligand hydrogen bonding is the same as that of ligand B in the present structure. The O···O hydrogen bond distances reported for the 1:1 complex are all within 0.05 Å of those found here for ligand B.

To our knowledge, this is the first reported X-ray crystal structure of a second-sphere complex involving a *natural* ionophore. It is also the first structure in which *three* carboxylic ionophores are bound to the same cation. As in structures of complexes of carboxylic ionophores with "bare" metal cations, the LAS ligands surround the cation with polar groups directed inward, thus creating a hydrophobic exterior that permits the large, trivalent cation to be dissolved in solvents of low polarity. It is anticipated that other natural, carboxylic ionophores will form similar complexes with inorganic ammines.

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Supplementary Material Available: Tables of bond distances, bond angles, torsion angles, anisotropic thermal parameters, and fractional coordinates and isotopic thermal parameters for hydrogen atoms (23 pages); a table of observed and calculated structure factor amplitudes (47 pages). Ordering information is given on any current masthead page.

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Models for Cytochrome P450 Prosthetic Heme Alkylation. Reaction of Diazoacetophenone with (Tetraphenylporphyrinato)iron(II) Chloride

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The reaction of diazoacetophenone with (tetraphenylporphyrinato)iron(II) yields [*N*-(2-phenyl-2-oxoethyl)tetraphenylporphyrinato]iron(II) chloride. The structure of this product has been established by spectroscopic methods and by X-ray crystallography. The crystal structure shows that the first carbon of the *N*-alkyl group is 2.94 Å from the iron atom and that the oxygen of the *N*-alkyl group points away from the iron. No evidence is seen for the Fe–C–N product expected from insertion of the diazo carbon into the metalloporphyrin iron–nitrogen bond or for intermediates in which the oxygen of the *N*-(2-phenyl-2-oxoethyl) group is coordinated to the iron. These results suggest it is unlikely that carbene-insertion or oxygen-coordinated intermediates will be detected during the N-alkylation of cytochrome P450 by diazo ketones. The results also rationalize the failure to detect iron-chelated enol species during N-alkylation of the prosthetic group of cytochrome P450 by catalytically activated phenylacetylene.

The cytochrome P450 catalyzed reduction of polyhalogenated hydrocarbons gives rise to semistable complexes with Soret bands at 450–490 nm.[1-3] Thus, enzymatic reduction of carbon tetrachloride yields a species with a Soret band at 460 nm believed to be the complex of dichlorocarbene with the ferrous prosthetic heme group ($Fe{=}CCl_2$).[1] The feasibility of this structural assignment is supported by the chemical synthesis and characterization of the (tetraphenylporphyrinato)iron(II)–dichlorocarbene complex.[4,5] The reduction of halothane (2,2,2-trifluoro-1-chloro-1-bromoethane) by cytochrome P450 yields a complex with a Soret band at 470 nm. This was first thought to be the analogous 2,2,2-trifluoroethylcarbene–iron complex, in part because the reaction of cytochrome P450 with 1,1,1-trifluoro-2-diazoethane yields a complex with a very similar Soret maximum (468 nm).[6,7] However, studies of the complex formed in the reaction of halothane with (tetraphenylporphyrinato)iron(II),[8] of the halocarbons produced when the cytochrome P450 complex decomposes,[9] and of the EPR properties of the model and enzymatic complexes[3] have led to the revised proposal that halothane yields a complex in which the 2,2,2-trifluoro-1-chloroethyl anion is coordinated to the prosthetic heme iron atom. Key support for this structural revision is provided by EPR evidence that the halothane complexes are low-spin paramagnetic (ferric) species whereas the putative carbene complexes are low-spin diamagnetic (ferrous) species.[3] The formation of carbene–iron and σ-bonded alkyl–iron complexes in the chemical reactions of ferrous porphyrins with halocarbons thus provides indirect support for the formation of similar types of complexes in the reductive reactions of cytochrome P450 with halocarbons.

The oxidation of a 3-((arylthio)ethyl)-4-methylsydnone by cytochrome P450 was recently shown to result in the formation of pyruvic acid and *N*-vinyl heme.[10] *N*-Vinyl heme formation is readily rationalized by enzymatic oxidation of the sydnone to a diazoalkane, insertion of the diazoalkane into one of the iron–nitrogen bonds of the heme group, and intramolecular β-elimination of the thioaryl moiety. This process occurs without the

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