the enol ether **108** as a 5:3 mixture of cis and trans isomers (**108a**:**108b**). Enol ether **108a**: ^{1}H NMR (CDCl$_3$) δ 1.62 (s, 6 H), 2.01 (m, 2 H), 2.09 (t, 2 H, J = 6.3 Hz), 2.70 (s, 2 H), 3.54 (s, 3 H), 5.78 (s, 1 H). Enol ether **108b**: ^{1}H NMR (CDCl$_3$) δ 1.62 (s, 6 H), 2.01 (m, 2 H), 2.33 (t, 2 H, J = 6.3 Hz), 2.47 (s, 2 H), 3.53 (s, 3 H), 5.87 (s, 1 H); IR (CHCl$_3$), (mixture of **108a** and **108b**) 2480 w, 2400 m, 2330 w, 1120 s, 1100 m, and 900 s cm^{-1}. The identity of the enol ethers was confirmed upon acid hydrolysis of the mixture to give a single compound which had an ^{1}H NMR spectrum identical to that for the aldehyde **109**. A similar treatment of the chromium complex **43** gave a 71% yield of **108**.

Reaction of 43 and 44 with Diazomethane. Diazomethane was generated in ether at 0 °C by shaking *N*-methyl-*N*-nitrosourea with 40% aqueous KOH. A large excess of diazomethane was prepared (10 equiv) and added to a solution of 0.138 g (0.401 mmol) of the chromium complex **43** in 10 mL of ether containing 0.32 mL (10 equiv) of pyridine. After 15 min at room temperature the reaction was complete and the excess diazomethane was swept with a stream of nitrogen into an acetic acid trap. The solvents were removed, and the residue was flash chromatographed on silica gel with a mixture of ether, methylene chloride, and hexane (1:1:20) to give 0.0522 g (0.314 mmol, 78%) of the enol ether **107**: ^{1}H NMR (CDCl$_3$) δ 1.50 (m, 1 H), 1.61 (s, 6 H), 1.85 (m, 1 H), 1.9-2.1 (m, 4 H), 2.25 (m, 1 H), 3.54 (s, 3 H), 3.84 (s, 1 H), 3.87 (s, 1 H); mass spectrum, *m/e* (rel intensity) 166 M$^+$ (11), 151 (18), 119 (22), 91 (29), 67 (32), 43 (100). The identity of **107** was confirmed upon acid hydrolysis to give a compound which had a ^{1}H NMR identical with that of the cycloadduct of methyl vinyl ketone and 2,3-dimethyl-1,3-butadiene. A similar reaction of the tungsten complex **44** gave an 80% yield of **107**.

Reaction of 43 with Hydrogen. A solution of 0.190 g (0.551 mmol) of the chromium complex **43** in 25 mL of hexane was deoxygenated with three freeze-thaw cycles (−190 °C to 25 °C), filled with argon, transferred to a Parr bomb, and then heated at 160 °C for 2.6 days under 1000 psi of hydrogen. The resulting mixture was filtered through Celite, concentrated, and flash chromatographed with a mixture of ether, methylene chloride and hexane (1:1:30) to give a 71% of the methyl ether **106**. Spectral data for **106**: ^{1}H NMR (CDCl$_3$) δ 1.2 (m, 1 H), 1.6 (s, 6 H), 1.65-2.1 (m, 6 H), 3.24 (dd, 2 H, J = 1.7 Hz, 6.6 Hz), 3.34 (s, 3 H); IR (CHCl$_3$) 2900 s, 1445 m, 1380 m, 1105 s, 950; mass spectrum, *m/e* (rel intensity) 154 M$^+$ (5), 123 (3), 122 (28), 121 (10), 107 (10). The identity of the ether **106** was confirmed by an independent synthesis. The Diels-Alder adduct of acrolein and 2,3-dimethyl-1,3-butadiene was reduced with sodium borohydride. The resulting alcohol was methylated with potassium hydride and methane fluorosulfonate to give a compound that had an identical ^{1}H NMR spectrum and GC retention time as the ether **106**. A second product (18% GC yield) was also obtained from the reaction of **43** with hydrogen and may correspond to the further reduction of the double bond in **106**. Although the reaction conditions were sufficient for complete conversion of **43**, no attempt was made to optimize the conditions for **106**.

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Communications to the Editor

Supramolecular Transport of Metal Complexes. Chiroselective Membrane Transport of Metal Amine Complexes by a Polyether Ionophore, Lasalocid A

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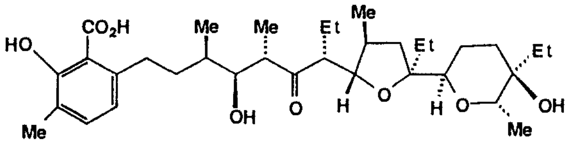
Lasalocid A (**1**) is a naturally occurring carboxylic ionophore that has been demonstrated to assist the transport of metal ions as well as amine cations across hydrophobic membranes.[1-3] It has been proposed for such systems that the anionic form of the antibiotic forms a complex with the cation to be transported such that the adduct has a hydrophobic exterior. More recently, outer-sphere complexes of lasalocid A and a number of metal ammine complexes have been isolated.[4,5] The X-ray structure of one such species, $[Co(NH_3)_6\cdot(\text{lasalocid A})_3]$, shows that three lasalocid anions in cyclic conformations (maintained by intraligand hydrogen bonds) surround the cobalt species such that the overall geometry is approximately spherical. As a consequence of its hydrophobic outer surface, the species is soluble in nonpolar solvents such as chloroform. The lasalocid A/cobalt ammine complex interactions involve a network of hydrogen bonds. These investigations parallel other recent studies[6,7] documenting related



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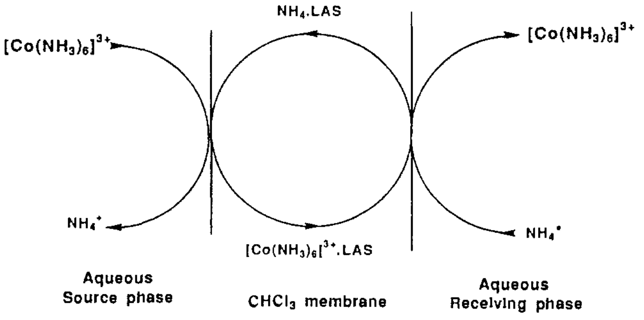

Figure 1. Lasalocid A anion (LAS) mediated transport of $[Co(NH_3)_6]^{3+}$ across a CHCl$_3$ membrane coupled to an NH$_4^+$ countergradient.

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Table I. Results of Lasalocid-Mediated Transport of Co(III) Amine Complexes through a $CHCl_3$ Bulk Liquid Membrane after 6 h at 25 °C

complex	initial source phase concn/10^{-3} mol dm^{-3}	av flux rate/10^{-4} mmol h^{-1} cm^{-2}	% enantiomeric purity (receiving phase)	% transport
2	10.0[a]	4.3 ± 0.1[b]		6.3
3[c]	20.0[d]	5.9 ± 0.8	10 ± 1[e]	4.3
4[c]	20.0[f]	7.1 ± 0.3	27 ± 4[g]	5.2

[a] The initial pH was 6.0, rising to 6.8 at the completion of the run. [b] Mean and average deviation from three separate runs. [c] Racemic mixture. [d] Initial pH 5.9. [e] Corresponds to 55% Δ isomer, 45% Λ isomer. [f] Initial pH 5.5. [g] Corresponds to 36.5% Δ isomer, 63.5% Λ isomer.

host–guest adduct formation between ammine complexes and crown polyethers.

Lasalocid A has also been employed previously for the optical resolution of chiral amines by fractional crystallization of their lasalocid salts.[8] Similarly, synthetic chiral macrocycles have been used as ionophores for the selective enantiomeric recognition and transport of a number of optically active guests such as asymmetric ammonium ions.[9,10] The aim of the present project was to investigate the potential of lasalocid A as an ionophore for the transport of inert metal complexes such as $[Co(NH_3)_6]Cl_3$ (**2**), $[Co(1,2\text{-diaminoethane})_3]Cl_3$ (**3**), and *u-cis*-$[Co(\text{diethylenetriamine})_2](ClO_4)_3$ (**4**). In addition, the prospect of achieving chiroselective transport of the latter two complexes was of especial interest.

Successful transport of the Co(III) complexes **2–4** was achieved by using a system involving aqueous source and receiving phases separated by a chloroform phase containing a 1 mM concentration of the ionophore as its sodium salt.[11] The arrangement used for the transport of $[Co(NH_3)_6]Cl_3$ (**2**) is illustrated in Figure 1, and details of the experiment are summarized in Table I; it should be noted that, given sufficient time, transport proceeds to completion.

For **3** and **4**, a racemic mixture of the respective complex (total concentration 20 mM) was present in the source phase at the beginning of each transport run. Details of the experiments, which were terminated after 6 h, are also summarized in Table I. At the end of these experiments, partial resolution of the complex in the receiving phase was observed in each case. For **3**, the observed optical rotation of the receiving phase corresponded to 55% of the Δ isomer and 45% of the Λ isomer being present.[12] For **4**, the resolution was greater, with 36.5% of the Δ isomer and 63.5% of the Λ isomer occurring in the source phase. In each case, the measured optical rotation of the source phase at the end of the experiment was of equivalent magnitude but opposite in sign to that measured for the corresponding receiving phase, thus confirming the internal consistency of the individual experiments.

Apart from its considerable intrinsic interest, the differential transport of intact metal complexes across bulk hydrophobic membranes provides a new technique for the separation of such species. In particular, the present study demonstrates that the procedure has special promise for the (partial) resolution of suitable optically active metal complexes. The latter remains a classical requirement in coordination chemistry that is not always readily met by conventional methods.

Acknowledgment. We thank the Australian Research Council for support and Associate Professor F. R. Keene for helpful discussions. G.W.E. is grateful for the hospitality extended to him at James Cook University during a recent sabbatical leave.

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(7) Very recently, crown ether ionophores incorporating proton-ionizable groups have been shown to facilitate the hydrophobic membrane transport of Co(II) and Ni(II) from a source phase consisting of ammonium hydroxide (pH 12). The evidence indicated that transport to the acid receiving phase involved adduct formation between the crown ionophore and the respective metal(II) ammine species. See: Strzelbicki, J.; Charewicz, W. A.; Liu, Y.; Bartsch, R. A. *J. Inclusion Phenom.* **1989**, *7*, 349.

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(11) The cell design was based on that of Di Casa et al.: Di Casa, M.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Tundo, P. *Inorg. Chem.* **1985**, *24*, 1610. The interfacial area (for each half of the cell) was 4.9 ± 0.5 cm^2. The volume of each phase was 20 mL, each phase was stirred independently, and the temperature was maintained at 25 ± 0.1 °C. For all experiments, the receiving phase was 0.1 mol dm^{-3} in ammonium chloride.

(12) Measured rotations were converted to enantiomeric purity by using the specific rotation measured for the levo isomer of $[Co(1,2\text{-diaminoethane})_3]I_3$ in 0.1 M NH_4Cl $\{[\alpha]^{25}{}_{436} = +1512 \pm 4°\}$. By way of example, a typical observed rotation at 436 nm for the receiving phase in a 10-cm cell was +0.029 ± 0.002°; the enantiomeric purities derived from measurements at four other wavelengths, although of lower accuracy since smaller rotations were involved, were still within experimental error of the value quoted in Table I. The specific rotation for *u-cis*-$[Co(\text{diethylenetriamine})_2](ClO_4)_3$ at (546 nm) was taken from the following: Keene, F. R.; Searle, G. H. *Inorg. Chem.* **1972**, *11*, 148. Once again, enantiomeric purity derived from measurements at other wavelengths agreed within experimental error with the value quoted in Table I.

Synthesis and Structural Characterization of the Cyclic Species $[GeN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$: The First "Germanazene"

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Inorganic cyclic systems that involve potentially delocalized, multiply bonded rings have been known for many years.[1] Perhaps the best known examples are borazine,[2] the cyclic phosphazenes,[3] certain cyclic sulfur nitrogen compounds,[4] and homocyclic cations of S, Se, or Te.[5] Recent additions have included the cyclic six-membered rings based upon B_3P_3[6] and Al_3N_3[7] skeletons and the cyclopentadiene-like P_5^- ion.[8] Oddly, there do not appear to be any stable counterparts of these compounds that involve the heavier main group 4 elements Si–Pb as an integral part of an unsaturated system for which a classical quasi-aromatic bonding model is possible.[9] In this paper, the first synthesis and characterization of such a compound, the trimeric species $(GeNAr)_3$ (where Ar = $2,6\text{-}i\text{-}Pr_2C_6H_3$) (**1**), is described.

The title compound **1** was synthesized by the treatment of $Ge[N(SiMe_3)_2]_2$[10] with H_2NAr[11] as follows: $Ge[N(SiMe_3)_2]_2$

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