with a radial distortion parameter ($\rho \simeq 19$ pm) that is only slightly larger than the one for $[NiL_2]^{3+}$. Such a phenomenon of a "planar dynamics" of an "antiferrodistortive order of elongated octahedra" (static, cooperative case) is well-known in the stereochemistry of d^9, d^4, and low-spin d^7 cations with E_g ground states, in particular for Cu^{2+}.[16] This sort of dynamic or nonresolved antiferrodistortive order should result in thermal ellipsoids of four nitrogen ligator atoms that are strongly elongated along the corresponding Ni–N bonds, however, as observed for the $[Cu(NO_2)_6]^{4-}$ entity in the β'-modification of $Cs_2PbCu(NO_2)_6$, for example.[20] Analogous efects are not found for $[Ni(bpy)_3](ClO_4)_3 \cdot 2CH_3CN \cdot 0.5CH_2Cl_2$. Presumably, the static compression in the solid state is stabilized by energetically efficient steric ligand or packing effects. As is well-known from the potential energy surface, which results from the vibronic coupling of an electronic E ground state with the vibrational ϵ-mode, the energy difference between an elongated and compressed D_{4h} geometry is not very large.[16] EPR spectroscopy, in particular on single crystals, would be the probe technique of choice for a final experimental decision. The **g** tensor of a compressed octahedron ($d_{x^2-y^2}$ ground state)[18]

$$g_\parallel' = g_0 + 8\mu + 2\mu' \qquad g_\perp' = g_0 + 2\mu + 2\mu' \tag{3}$$

(see the short-hand notations in eq 1 has the sequence of g values $g_\parallel' > g_\perp' > g_0$, in contrast to $g_\perp > g_\parallel \geq g_0$ for the elongated octahedron (eq 1). In case of a "planar dynamics" or an antiferrodistortive order of elongated octahedra with exchange-coupled **g** tensors, the following averaged g values are expected:

$$\begin{aligned} \bar{g}_\parallel &= g_\perp = g_0 + 6\mu + 2\mu' \\ \bar{g}_\perp &= \tfrac{1}{2}(g_\parallel + g_\perp) = g_0 + 3\mu + 2\mu' \end{aligned} \tag{4}$$

Though the sequence $\bar{g}_\parallel > \bar{g}_\perp$ g_0 is the same as for a $d_{x^2-y^2}$ ground state, the orbital contribution μ to the g values are rather different in the two cases (eq 2 and 3). Because the contribution μ', resulting from the singlet–triplet separation, is rather small in case of nitrogen as the ligator atom (see above), it should be possible to distinguish between the cases represented by eq 2 and 3 by carefully checking the deviations of the g values for g_0. For Cu^{2+} this can indeed easily be done.[16] Finally, it should be mentioned that for Co^{2+} in octahedral coordination, which is also low-spin in the presence of strong ligands, a d_{z^2} ground state and an elongated coordination are well established,[21] in correspondence to the case of Ni^{3+}.

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Registry No. $[NiL_2](ClO_4)_3$, 86709-82-2; $[NiL_2]_2(S_2O_6)_3 \cdot 7H_2O$, 101630-19-7.

Supplementary Material Available: Listings of thermal parameters, positional parameters of hydrogen atoms, and C–C and C–N bond lengths (4 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (17 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, FRG,
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Macrocyclic Complexes of Indium(III): Novel μ-Hydroxo- and μ-Oxo-Bridged Complexes. Crystal Structures of $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$ and $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)] \cdot 2NaClO_4$ (L = 1,4,7-Triazacyclononane)

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Indium(III) chloride reacted with the macrocyclic ligands (1:1) 1,4,7-triazacyclononane (L), 1,4,7-trimethyl-1,4,7-triazacyclononane (L′), and 1,4,7-trithiacyclononane (L″) in chloroform (acetonitrile) to yield at 60 °C the complexes $LInCl_3$, $L'InCl_3$, and $L''InCl_3$, respectively. $LInBr_3$ was prepared analogously in aqueous solution. Hydrolysis of $LInBr_3$ in alkaline aqueous solution afforded the colorless, tetrameric cation $[L_4In_4(\mu\text{-}OH)_6]^{6+}$, the first well-characterized μ-hydroxo complex of indium(III), which has been isolated as the perchlorate, dithionate, iodide, and hexafluorophosphate salts, respectively. $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 14.56$ (1) Å, $b = 16.38$ (1) Å, $c = 25.09$ (2) Å, $V = 5983.8$ Å^3, and $d_{calcd} = 1.810$ g cm^{-3} for $Z = 4$ and molecular weight 1630.6. Least-squares refinement of the structure based on 4293 observations led to a final discrepancy index of $R = 0.074$. The structure consists of discrete tetrameric cations and dithionate anions. The $In_4(OH)_6$ core has an adamantane-like skeleton. The average In–O bond distance is 2.14 (1) Å. Hydrolysis of $LInBr_3$ in 2 M sodium acetate at 60 °C and addition of sodium perchlorate yielded colorless crystals of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)] \cdot 2NaClO_4$, which crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.445$ (6) Å, $b = 11.846$ (7) Å, $c = 14.986$ (9) Å, $\alpha = 76.22$ (5)°, $\beta = 67.94$ (5)°, $\gamma = 67.53$ (4)°, $V = 1729.4$ Å^3, and $d_{calcd} = 1.85$ g cm^{-3} for $Z = 2$ and molecular weight 985.1. Least-squares refinement of the structure based on 7713 reflections led to a final R value of 0.057. The structure consists of the neutral, μ-oxo-bridged dimer $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]$ and sodium perchlorate. The average In–O bond distance of the oxo bridge is 2.114 (4) Å.

Introduction

Recently, the hydrolysis of indium(III) in aqueous solution has been investigated by potentiometric titration at 25 °C in 0.1 M potassium nitrate.[2] The occurrence of the monomeric hydroxo species $InOH^{2+}$ and $In(OH)_2^+$ has been confirmed in this study, but species of higher nuclearity have also been proposed such as $In_p(OH)_p^{2p+}$. The best fit for a model with $p = 4$ has been obtained; e.g., a tetrameric μ-hydroxo-bridged species has been suggested to exist in aqueous solution at higher pH. A search of the literature revealed that—surprisingly enough—no well-defined μ-hydroxo-bridged complexes of indium(III) have been synthesized and characterized by X-ray crystallography.

We have in the past few years used a simple synthetic route to μ-hydroxo-bridged complexes of transition metals, which used monomeric complexes of the type LMX_3 (L represents small, tridentate macrocyclic, N-donor ligands and X^- is a monodentate ligand (Cl^-, Br^-)) as starting materials that undergo hydrolysis reactions in alkaline aqueous solution. Due to the inherent thermodynamic and kinetic stability of the LM moiety, in many cases no dissociation of the ligands L occurred and formation of various μ-hydroxo- and/or μ-oxo-bridged complexes (dimeric,[3]

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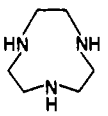
0020-1669/86/1325-1654$01.50/0

Table I. Crystallographic Data (22 °C)

formula	$[In_4(C_6H_{15}N_3)_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$	$[In_2(C_6H_{15}N_3)_2(\mu\text{-}O)(CH_3CO_2)_4] \cdot 2NaClO_4$
fw	1630.6	985.1
space group	$P2_12_12_1$	$P\bar{1}$
a, Å	14.56 (1)	11.445 (6)
b, Å	16.38 (1)	11.846 (7)
c, Å	25.09 (2)	14.986 (9)
α, deg	90	76.22 (5)
β, deg	90	67.94 (5)
γ, deg	90	67.53 (4)
V, Å^3	5983.8	1729.4
Z	4	2
d_{calcd}, g/cm^3	1.810	1.85
cryst size, mm^3	0.1 × 0.15 × 0.3	0.5 × 0.5 × 0.4
$\mu_{Mo\,K\alpha}$, cm^{-1}	16.7	14.4
transmissn factors, min–max	0.36–0.50	0.20–0.53
data collcn instrum	AEDII Siemens	AEDII Siemens
radiation (graphite monochromated)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
scan method	ω	ω
data collcn range (2θ), deg	2.5–60	2.5–57
no. of unique data ($I > 1.5\sigma(I)$)	4293	7713
no. of params refined	437	396
R; R_w	0.074; 0.063	0.057; 0.055

trimeric,[4] tetrameric,[5] and even octameric[6]) was observed.

We have now extended this concept to main-group metals, and we here wish to report the syntheses of $LInCl_3$, $L'InCl_3$ and $L''InCl_3$ as well as $LInBr_3$. The latter material proved to be very susceptible to hydrolysis reactions, and a tetrameric species $[L_4In_4(\mu\text{-}OH)_6]^{6+}$ has been isolated as the perchlorate, hexafluorophosphate, or iodide salt, respectively. The dithionate salt, $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$, gave colorless crystals suitable for X-ray crystallography. Hydrolysis in the presence of acetate ions and addition of sodium perchlorate yield the dimeric, μ-oxo-bridged neutral complex $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)] \cdot 2NaClO_4$. The crystal structures of both complexes are described in this work.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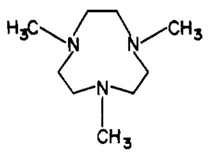
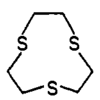

L'


L''

Experimental Section

The macrocyclic ligands 1,4,7-triazacyclononane (L),[3a] 1,4,7-trimethyl-1,4,7-triazacyclononane (L'),[7] and 1,4,7-trithiacyclononane (L'')[8] were prepared as described in the literature.

Preparation of Complexes. $LInCl_3$ and $L'InCl_3$. To a solution of $InCl_3$ (0.22 g, 1 mmol) in dry chloroform (40 mL) was added 1 mL of a 1 M ethanolic solution of the respective cyclic triamine (L, L'). This solution was refluxed for 2 h, after which time a colorless precipitate of $LInCl_3$ ($L'InCl_3$) was filtered off, washed with ethanol and ether, and air-dried (yield ~90%.)

Anal. Calcd for $C_6H_{15}N_3Cl_3In$: C, 20.56; H, 4.30; N, 11.99. Found: C, 20.3; H, 4.5; N, 12.1. Calcd for $C_9H_{21}N_3Cl_3In$: C, 27.5; H, 5.4; N, 10.7. Found: C, 27.5; H, 5.3; N, 10.5.

$L''InCl_3$. To a solution of $InCl_3$ (0.22 g, 1 mmol) in acetonitrile (40 mL) was added 1,4,7-trithiacyclononane (0.18 g). The solution was stirred for 30 min at 40 °C. A colorless precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 72%).

Anal. Calcd for $C_6H_{12}Cl_3InS_3$: C, 17.95; H, 3.01. Found: C, 18.0; H, 3.1.

$LInBr_3$. 1,4,7-Triazacyclononane trihydrobromide (0.37 g, 1 mmol) and indium(III) nitrate were dissolved in water (50 mL) at 60 °C. A solution of 0.1 M NaOH was added dropwise to this solution with stirring until the pH was adjusted to 4. A colorless precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 93%).

Anal. Calcd for $C_6H_{15}N_3Br_3In$: C, 14.89; H, 3.13; N, 8.68. Found: C, 14.7; H, 3.1; N, 8.8.

$[L_2In](ClO_4)_3 \cdot 2H_2O$. Indium nitrate (0.3 g), 1,4,7-triazacyclononane (0.3 g), and sodium acetate (0.5 g) were dissolved in dry methanol (40 mL) and refluxed for 48 h. To the clear solution was added $NaClO_4 \cdot H_2O$ (0.8 g). A colorless precipitate formed within 48 h, which was filtered off (yield 50%).

Anal. Calcd for $[C_{12}H_{30}N_6In](ClO_4)_3 \cdot 2H_2O$: C, 20.38; H, 4.84; N, 11.88; ClO_4, 42.19. Found: C, 20.5; H, 4.6; N, 12.0; ClO_4, 42.2.

$[L_4In_4(\mu\text{-}OH)_6](ClO_4)_6 \cdot 6H_2O$. To a suspension of $InBr_3$ (0.48 g, 1 mmol) in water (40 mL) was added aqueous sodium hydroxide (1 M) dropwise with stirring until a clear, colorless solution (pH ~8) was obtained, to which $NaClO_4 \cdot H_2O$ (2 g) was added. After the mixture was allowed to stand for 12 h in an open vessel at room temperature, colorless crystals formed, which were filtered off and air-dried (yield 79%).

Anal. Calcd for $(C_6H_{15}N_3In)_4(OH)_6(ClO_4)_6 \cdot 6H_2O$: C, 16.17; H, 4.41; N, 9.42; ClO_4, 33.47. Found: C, 16.2; H, 4.2; N, 9.3; ClO_4, 33.3.

$[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$. The dithionate salt was obtained by the above procedure using sodium dithionate dihydrate (2 g) instead of sodium perchlorate monohydrate. Colorless crystals of X-ray quality were grown from such solutions within 3 days.

Anal. Calcd for $(C_6H_{15}N_3)_4In(OH)_6(S_2O_6)_3 \cdot 4H_2O$: C, 17.68; H, 4.57; N, 10.31. Found: C, 17.5; H, 4.3; N, 10.1. An analogous iodide salt (tetrahydrate) and a hexafluorophosphate salt (pentahydrate) were obtained with NaI and $NaPF_6$, respectively, which also gave satisfactory elemental analyses.

$[(LIn(CH_3CO_2)_2)_2O] \cdot 2NaClO_4$. $LInBr_3$ (0.48 g, 1 mmol) was dissolved in 2 M aqueous sodium acetate (40 mL) at 60 °C. Sodium perchlorate monohydrate (2 g) was added. Within 1 week colorless crystals of X-ray quality formed from this solution at room temperature in an open vessel, which were filtered off, washed rapidly with ethanol and ether, and air-dried (yield 81%).

Anal. Calcd for $C_{30}H_{42}N_6O_9In_2 \cdot 2NaClO_4$: C, 24.38; H, 4.29; N, 8.53; ClO_4, 20.19; Na, 4.67. Found: C, 24.5; H, 3.9; N, 8.6; ClO_4, 20.6; Na, 4.9.

$[L_2In_2(\mu\text{-}SH)_3]Br_3 \cdot H_2O$. $LInBr_3$ (0.48 g, 1 mmol) was dissolved in aqueous 2 M ammonia at 60 °C. Through the clear solution was passed a stream of gaseous H_2S slowly for 10 min. Addition of sodium bromide (3 g) initiated the precipitation of a colorless solid material, which was filtered off, washed with ethanol and ether, and air-dried.

Anal. Calcd for $C_{12}H_{33}N_6Br_3In_2S_3 \cdot H_2O$: C, 17.06; H, 4.17; N, 9.95; S, 11.38; Br, 28.32. Found: C, 17.2; H, 4.1; N, 9.9; S, 11.4; Br, 28.4.

A triperchlorate dihydrate salt was prepared analogously from sodium perchlorate monohydrate (3 g) instead of sodium bromide.

X-ray Structural Determinations. Colorless crystals of $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$ and of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)] \cdot 2NaClO_4$ were attached to the end of glass fibers and mounted on an AED II Siemens diffractometer, respectively. Unit cell dimensions at ambient temperature

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Table II. Atomic Coordinates of $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3\cdot4H_2O$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
In1	0.2730 (1)	0.3804 (1)	0.39589 (7)	N41	0.616 (1)	0.594 (1)	0.3546 (7)
In2	0.2922 (1)	0.6122 (1)	0.43569 (7)	N42	0.598 (1)	0.428 (1)	0.3110 (8)
In3	0.2776 (1)	0.5488 (1)	0.28696 (7)	N43	0.610 (1)	0.456 (1)	0.4262 (8)
In4	0.4985 (1)	0.4998 (1)	0.36811 (7)	C19	0.675 (2)	0.564 (1)	0.315 (1)
O1	0.2379 (10)	0.4900 (8)	0.4368 (5)	C20	0.643 (2)	0.496 (2)	0.284 (1)
O2	0.258 (1)	0.626 (1)	0.3541 (5)	C21	0.667 (2)	0.390 (1)	0.3459 (9)
O3	0.257 (1)	0.426 (1)	0.3165 (6)	C22	0.640 (2)	0.370 (1)	0.4054 (10)
O4	0.418 (1)	0.3998 (10)	0.3931 (8)	C23	0.686 (1)	0.518 (1)	0.4294 (8)
O5	0.436 (1)	0.5772 (8)	0.4264 (6)	C24	0.660 (1)	0.597 (1)	0.4125 (9)
O6	0.424 (1)	0.5440 (9)	0.2996 (6)	S1	0.4810 (6)	0.2604 (5)	0.2444 (3)
N11	0.127 (1)	0.320 (1)	0.3972 (9)	S2	0.4498 (8)	0.3074 (5)	0.1678 (3)
N12	0.127 (1)	0.245 (1)	0.3614 (9)	O11	0.469 (1)	0.176 (1)	0.2406 (8)
N13	0.288 (1)	0.301 (1)	0.4734 (9)	O12	0.424 (1)	0.304 (1)	0.282 (1)
C13	0.118 (1)	0.279 (2)	0.356 (1)	O13	0.548 (1)	0.288 (1)	0.2497 (9)
C14	0.190 (2)	0.222 (2)	0.354 (1)	O21	0.355 (2)	0.278 (2)	0.166 (1)
C15	0.344 (2)	0.206 (1)	0.400 (1)	O22	0.461 (1)	0.386 (1)	0.170 (1)
C16	0.312 (2)	0.216 (1)	0.456 (1)	O23	0.518 (1)	0.266 (1)	0.1301 (8)
C17	0.188 (2)	0.316 (2)	0.492 (1)	S3	0.4474 (5)	0.4098 (4)	0.5576 (3)
C18	0.110 (2)	0.288 (2)	0.452 (1)	S4	0.5414 (5)	0.5096 (5)	0.5676 (3)
N21	0.344 (1)	0.747 (1)	0.4510 (9)	O31	0.459 (1)	0.358 (1)	0.6032 (7)
N22	0.155 (1)	0.672 (1)	0.4626 (7)	O32	0.474 (1)	0.372 (1)	0.5058 (6)
N23	0.306 (1)	0.614 (1)	0.5264 (6)	O33	0.352 (1)	0.446 (1)	0.5534 (6)
C1	0.402 (1)	0.740 (1)	0.4977 (10)	O41	0.518 (1)	0.546 (1)	0.6193 (8)
C2	0.250 (1)	0.798 (1)	0.4584 (10)	O42	0.629 (2)	0.470 (1)	0.5658 (9)
C3	0.155 (2)	0.756 (1)	0.440 (1)	O43	0.525 (1)	0.562 (1)	0.5208 (6)
C4	0.152 (1)	0.666 (1)	0.5242 (10)	S5	−0.0368 (6)	0.4954 (6)	0.4626 (4)
C5	0.220 (2)	0.608 (2)	0.5490 (9)	S6	−0.0294 (6)	0.5492 (6)	0.3882 (4)
C6	0.356 (2)	0.696 (2)	0.542 (1)	O51	−0.101 (2)	0.548 (2)	0.498 (1)
N31	0.125 (1)	0.552 (1)	0.2601 (8)	O52	−0.080 (1)	0.416 (2)	0.4546 (9)
N32	0.278 (1)	0.494 (1)	0.2019 (8)	O53	0.062 (2)	0.490 (1)	0.4818 (9)
N33	0.272 (2)	0.662 (1)	0.2302 (8)	O61	0.010 (1)	0.629 (2)	0.3921 (9)
C7	0.116 (1)	0.486 (1)	0.223 (1)	O62	0.032 (1)	0.487 (2)	0.3540 (9)
C8	0.108 (2)	0.638 (2)	0.244 (1)	O63	−0.120 (2)	0.544 (1)	0.370 (1)
C9	0.176 (2)	0.690 (2)	0.230 (2)	O_w1	0.230 (2)	0.206 (1)	0.8318 (7)
C10	0.308 (2)	0.634 (1)	0.174 (1)	O_w2	0.221 (3)	0.300 (2)	0.238 (1)
C11	0.318 (2)	0.550 (1)	0.168 (1)	O_w3	0.424 (3)	0.164 (2)	0.819 (1)
C12	0.185 (2)	0.463 (2)	0.186 (1)	O_w4	0.410 (1)	0.982 (1)	0.386 (1)

(22 °C) were obtained by a least-squares fit of the setting angles of 30 reflections, respectively. The data are summarized in Table I together with details of intensity measurements. Intensity data were corrected in the usual manner for Lorentz and polarization effects; empirical corrections for absorption were carried out[9] in both cases. The structure of the tetrameric complex was solved by direct methods, whereas conventional Patterson and Fourier techniques were used to solve the structure of the μ-oxo-bridged dimeric complex. Idealized positions of the methylene H atoms were calculated and were not refined in both cases. All other H atoms have not been included. All non-hydrogen atoms were refined with use of anisotropic thermal parameters for $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot2NaClO_4$ except the oxygen atoms of the ClO_4^- anions and of the water of crystallization, for which isotropic thermal parameters were refined.

In the $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3\cdot4H_2O$ structure the indium nitrogen, sulfur, and oxygen atoms of the hydroxo bridges were refined with anisotropic thermal parameters only.

The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence factors $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = [\sum w_i(|F_o| - |F_c|)^2/\sum w_i|F_o|^2]^{1/2}$ as given in Table I where $w_i = 1/\sigma(I)^2$. Scattering factors for neutral atoms were taken from ref 10. The real and imaginary parts of anomalous dispersion for all non-hydrogen atoms were included. The final atomic parameters for $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3\cdot4H_2O$ are given in Table II and those of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot2NaClO_4$ in Table III. Selected bond distances and angles are listed in Tables IV and V. Listings of anisotropic thermal parameters and calculated coordinates of H atoms are available as supplementary material for both structures.

Results and Discussion

Preparation of Complexes. The reaction of indium(III) chloride dissolved in chloroform with the tridentate, macrocyclic ligands 1,4,7-triazacyclononane (L) and 1,4,7-trimethyl-1,4,7-triazacyclononane (1:1) at 60 °C yielded colorless solid materials of the composition $LInCl_3$ and $L'InCl_3$, respectively. A similar complex, $LInBr_3$, was obtained from aqueous solutions of indium(III) nitrate and 1,4,7-triazacyclononane trihydrobromide after the pH was adjusted to 4 with sodium hydroxide. The reaction of the sulfur-containing compound 1,4,7-trithiacyclononane with $InCl_3$ in acetonitrile gave colorless $L''InCl_3$. Octahedral complexes of indium(III) with an InN_6 or InN_3X_3 (X = Cl, Br) are quite common in the coordination chemistry of indium(III).[11] In all these cases the tridentate macrocycle occupies one face of an octahedral In(III) ion, and consequently, the three halide ligands are also facially coordinated. In InX_3(terpy) (terpy = 2,2′,2″-terpyridyl) a meridional arrangement of the halide ligands is enforced by the tridentate N-donor ligand 2,2′,2″-terpyridyl.[12] In the infrared spectrum in the range 200–600 cm^{-1} (Nujol mull, CsI disks), In–Cl stretching frequencies were observed at 257, 271, and 269 cm^{-1} for $LInCl_3$, $L'InCl_3$, and $L''InCl_3$, respectively. Of the two ν(M–X) infrared-active modes expected for C_{3v} symmetry only one is observed in all instances. These are in the region observed for other InX_3L_3 species.[13] We have not been able to identify the ν(In–Br) modes in $LInBr_3$ in the region 200–600 cm^{-1}. When the ratio of 1,4,7-triazacyclononane to indium was 2:1, the colorless cation $[InL_2]^{3+}$ formed, which was isolated as $[InL_2](ClO_4)_3\cdot2H_2O$ from aqueous solution.

Subsequently, we have used $LInBr_3$ as starting material for hydrolysis reactions in the presence and absence of other coordinating, possibly bridging ligands. Thus, the reaction of $LInBr_3$ in water at 60 °C and dropwise addition of sodium hydroxide until the pH remained constant at 8 yielded a clear colorless solution. Interestingly, no precipitation of $In(OH)_3$ was observed at any

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(9) All computations were carried out with the program system STRUCSY: *Structure System Program Package*; Stoe: Darmstadt, Federal Republic of Germany, 1984.

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Table III. Atomic Coordinates of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot 2NaClO_4$

atom	*x*	*y*	*z*
In1	0.16598 (4)	0.27414 (4)	0.157772 (3)
N11	0.3526 (5)	0.3242 (5)	0.1220 (4)
N12	0.0956 (5)	0.4821 (5)	0.1156 (4)
N13	0.1298 (5)	0.3545 (5)	0.2956 (3)
C11	0.3350 (8)	0.4350 (8)	0.0458 (7)
C12	0.2049 (9)	0.5254 (7)	0.0669 (8)
C13	0.012 (1)	0.5354 (8)	0.2079 (7)
C14	0.0548 (9)	0.4862 (6)	0.2910 (6)
C15	0.2675 (9)	0.3260 (9)	0.2990 (6)
C16	0.3669 (8)	0.3487 (10)	0.2070 (7)
O1	0.2620 (5)	0.1908 (4)	0.0253 (3)
O2	0.0901 (6)	0.3228 (5)	−0.0119 (4)
C1	0.1928 (7)	0.2384 (6)	−0.0320 (5)
C2	0.2502 (9)	0.1855 (8)	−0.1289 (6)
O3	0.1986 (4)	0.1002 (3)	0.2498 (3)
O4	0.4122 (4)	0.0462 (4)	0.1638 (3)
C3	0.3162 (6)	0.0220 (5)	0.2276 (5)
C4	0.3333 (8)	−0.1057 (6)	0.2822 (6)
In2	−0.18961 (4)	0.23519 (4)	0.31500 (3)
N21	−0.3333 (5)	0.1348 (4)	0.4192 (3)
N22	−0.0510 (4)	0.0381 (5)	0.3384 (4)
N23	−0.2132 (5)	0.1280 (4)	0.2150 (3)
C21	−0.2634 (6)	0.0134 (6)	0.4613 (5)
C22	−0.1163 (7)	−0.0050 (6)	0.4405 (5)
C23	−0.0337 (7)	−0.0395 (6)	0.2658 (5)
C24	−0.0803 (7)	0.0328 (7)	0.1830 (5)
C25	−0.3238 (6)	0.0756 (6)	0.2676 (5)
C26	−0.4106 (5)	0.1290 (6)	0.3608 (4)
O5	−0.1142 (4)	0.2756 (4)	0.4126 (3)
O6	−0.3178 (4)	0.3285 (4)	0.5186 (3)
C5	−0.1988 (6)	0.3194 (5)	0.4918 (4)
C6	−0.1448 (7)	0.3614 (7)	0.5514 (6)
O7	−0.3558 (5)	0.4014 (4)	0.3238 (4)
O8	−0.2834 (8)	0.4190 (8)	0.1710 (5)
C7	−0.3628 (7)	0.4560 (6)	0.2450 (6)
C8	−0.4777 (8)	0.5788 (7)	0.2420 (5)
O	−0.0341 (4)	0.2805 (4)	0.1977 (3)
Na1	0.50000 (0)	0.0000 (0)	0.0000 (0)
Na2	−0.50000 (0)	0.5000 (0)	0.5000 (0)
Cl1	0.2979 (2)	−0.1820 (1)	0.0381 (2)
O11	0.3362 (6)	−0.2519 (6)	−0.0404 (5)
O12	0.2602 (7)	−0.2519 (6)	0.1272 (5)
O13	0.4166 (7)	−0.1618 (6)	0.0324 (5)
O14	0.203 (1)	−0.0710 (9)	0.0302 (8)
Cl2	0.3198 (2)	0.2964 (1)	0.5770 (1)
O21	0.4094 (5)	0.1786 (5)	0.5945 (4)
O22	0.3922 (6)	0.3541 (6)	0.4870 (5)
O23	0.2904 (7)	0.3766 (7)	0.6428 (5)
O24	0.2092 (7)	0.2890 (6)	0.5674 (5)

Table IV. Selected Bond Distances (Å) and Angles (deg) of the Cation $[L_4In_4(\mu\text{-}OH)_6]^{6+}$

In1–O1	2.13 (1)	In2–O1	2.15 (1)
In1–O3	2.14 (1)	In2–O2	2.11 (1)
In1–O4	2.14 (1)	In2–O5	2.18 (1)
In1–N11	2.33 (2)	In2–N21	2.36 (2)
In1–N12	2.38 (2)	In2–N21	2.32 (1)
In1–N13	2.34 (2)	In2–N21	2.28 (1)
In3–O2	2.13 (2)	In4–O4	2.10 (1)
In3–O3	2.15 (2)	In4–O5	2.13 (1)
In3–O6	2.16 (1)	In4–O6	2.15 (1)
In3–N31	2.31 (2)	In4–N41	2.33 (2)
In3–N32	2.31 (2)	In4–N42	2.35 (2)
In3–N33	2.34 (1)	In4–N43	2.29 (2)
O1–In1–O3	97.1 (9)	O1–In1–N11	97 (1)
O1–In1–O4	97.3 (9)	O1–In1–N12	168 (6)
O3–In1–O4	91.2 (9)	O1–In1–N13	95 (1)
O3–In1–N11	94 (1)	O4–In1–N11	164 (5)
O3–In1–N12	90 (1)	O4–In1–N12	92 (1)
O3–In1–N13	167 (0.6)	O4–In1–N13	90 (1)
N11–In1–N12	72 (1)	N11–In1–N13	81 (1)
N12–In1–N13	77 (1)		
In1–O1–In2	133.6 (2)	In1–O4–In4	132.2 (2)
In1–O2–In3	131.7 (2)	In2–O5–In4	129.4 (2)
In1–O3–In3	129.5 (2)	In3–O6–In4	128.5 (2)

Table V. Selected Bond Distances (Å) and Angles (deg) of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot 2NaClO_4$

In1–O	2.114 (4)	In2–O	2.115 (4)
In1–O1	2.142 (5)	In2–O5	2.171 (5)
In1–O2	2.851 (6)	In2–O7	2.875 (8)
In1–O3	2.175 (5)	In2–O8	2.142 (5)
In1–N11	2.271 (5)	In2–N21	2.289 (5)
In1–N12	2.290 (5)	In2–N22	2.299 (5)
In1–N13	2.312 (5)	In2–N23	2.324 (5)
Na1–O1a	2.756 (5)	Na2–O6a	2.340 (5)
Na1–O4a	2.389 (5)	Na2–O7a	2.789 (6)
Na1–O13	2.330 (7)	Na2–O22	2.553 (7)
N11–In1–N12	77.1 (3)	N12–In1–N13	76.5 (3)
N11–In1–N13	77.1 (2)	N12–In1–O1	106.6 (3)
N11–In1–O1	86.5 (3)	N12–In1–O2	71.0 (2)
N11–In1–O2	109.7 (3)	N12–In1–O3	158 (1)
N11–In1–O3	104.9 (3)	N12–In1–O	87.9 (2)
N11–In1–O	164 (1)		
N13–In1–O1	162 (1)	O1–In1–O2	48.9 (2)
N13–In1–O2	143.8 (6)	O1–In1–O3	94.4 (3)
N13–In1–O3	83.4 (2)	O1–In1–O	104.2 (3)
N13–In1–O	93.3 (3)	O2–In1–O3	125.8 (4)
		O2–In1–O	70.5 (2)
		O3–In1–O	86.8 (2)
O1a–Na1–O4a	109.3 (3)	O1–Na1–O1a	178 (4)
O1a–Na1–O4a	70.6 (2)	O4–Na1–O4a	180 (5)
In1–O–In2	142.5 (2)		

stage of the reaction. Addition of sodium perchlorate monohydrate, sodium hexafluorophosphate, sodium iodide, and sodium dithionate dihydrate to this solution initiated the slow precipitation of colorless crystals, which were analyzed to consist of $[L_4In_4(\mu\text{-}OH)_6](ClO_4)_6\cdot 6H_2O$, $[L_4In_4(\mu\text{-}OH)_6](PF_6)_6\cdot 5H_2O$, $[L_4In_4(\mu\text{-}OH)_6]I_6\cdot 4H_2O$, and $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3\cdot 4H_2O$, respectively. The yields were quite satisfactory (~80% based on $LInBr_3$). In the infrared spectrum of the hexafluorophosphate salt a band at 3600 cm^{-1} was observed, which we assign to the ν(O–H) stretching mode of the μ-hydroxo bridge. Crystals of the dithionate salt were of X-ray quality (see below).

Hydrolysis of $LInBr_3$ in 2 M sodium acetate at 60 °C also gave a clear, colorless solution, from which upon addition of sodium perchlorate monohydrate colorless crystals of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot 2NaClO_4$ precipitated within 14 days. In the infrared spectrum strong bands at 1615 cm^{-1} (ν(C═O)) and 1380 and 1330 cm^{-1} (ν(C—O)) are indicative of monodentate acetato ligands. The crystal structure has been determined (see below).

Hydrolysis of $LInBr_3$ in aqueous ammonium ion (2 M) in the presence of HS^- ions (H_2S was passed through the solution) and addition of sodium perchlorate monohydrate or sodium bromide yielded colorless solid materials of the composition $[L_2In_2(SH)_3](ClO_4)_3\cdot 2H_2O$ or $[L_2In_2(SH)_3]Br_3\cdot H_2O$, respectively. We were so far unable to grow crystals suitable for X-ray crystallography. A dimeric or a tetrameric structure containing the cation $[L_4In_4(\mu\text{-}SH)_6]^{6+}$ in analogy to the μ-hydroxo-bridged species are conceivable.

It is noted that the ligand 1,4,7-triazacyclononane binds strongly to indium(III) even in aqueous solution. The stability of the LIn^{3+} moiety is remarkable because it survives even in alkaline, aqueous solution (pH 8–9) without precipitation of $In(OH)_3$.

Description of the Structure of $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3\cdot 4H_2O$. The structure of the cationic species is tetrameric. Figure 1 shows a perspective view and the atomic labeling scheme of the cation. The $In_4(\mu\text{-}OH)_6$ core has an adamantane-like skeleton: the four In atoms occupy the corners of a nearly regular tetrahedron, and the μ-OH bridges are located above the centers of the six edges of this tetrahedron. The In atoms are in a distorted octahedral

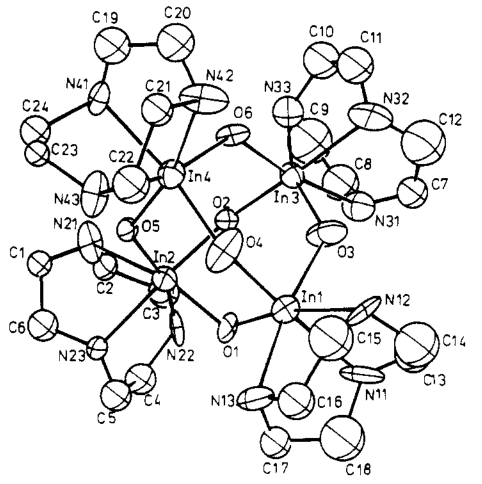

Figure 1. Perspective view of the cation $[L_4In_4(\mu\text{-}OH)_6]^{6+}$ and atomic labeling scheme.

environment of three facially coordinated N atoms of the macrocyle and three oxygen atoms of three μ-OH bridges. This structure type has recently been found in $[F_{12}Ta_4O_6]^{4-}$,[14] $[L_4Mn_4O_6]^{4+}$,[5b] and $[L_4Ti_4O_6]^{4+}$,[5a] all of which contain metal centers in high oxidation states (>III) and μ-oxo bridges. Recently, an organometallic complex, $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6](BF_4)_2$, has also been shown to have an adamantane-like $Cr_4(\mu\text{-}OH)_6$ core.[15]

The average In–O bond length is 2.144 Å. For $In(OH)_3$ an In–O bond length of 2.171 Å has been reported.[16] This structure is composed of $In(OH)_6$ octahedra and μ-OH bridges.

The average In–N bond distance is 2.334 Å. In $In(CH_3CO_2)_3(bpy)$ and $In(CH_3CO_2)_3(phen)$, where indium(III) is eight-coordinate, In–N bond lengths of 2.33 Å have been reported, respectively.[17] In $InCl_2(benz)(py)_2$ (benz = benzoate), a six-coordinate neutral complex, an average In–N distance of 2.28 Å has been observed;[18] the same value is observed in diaqua(2,6-diacetylpyridine semicarbazone)indium(III) hydroxide dinitrate,[19] which contains a seven-coordinate indium(III), and in dichloro-(acetylacetonato)-2,2′-dipyridylindium(III), with a six-coordinate In(III) center.[20] And finally, in indium(III) dithizonate, $In(Hdz)_3$, a five-coordinate complex of indium(III), two In–N bond distances of 2.372 (6) and 2.334 (6) Å have been reported.[21]

The InN_3O_3 octahedra in the tetrameric cation are quite distorted due to the steric constraints of the cyclic amine ligand leading to N–In–N angles <90° (average N–In–N bond angle 77.3°). An average O–In–O bond angle of 96.2° indicates considerable strain within the $In_4(\mu\text{-}OH)_6$ core. The average In–O–In bond angle is 130.8°, which may be compared with a Cr–O–Cr angle of 140° in $[(Me_5C_5)_4Cr_4(OH)_6](BF_4)_2$.[15] The N–C and C–C distances show no unusual features; the geometry of the coordinated 1,4,7-triazacyclononane rings is very similar to that of many other transition-metal complexes containing this ligand.[3-7]

The dithionate anions are well separated from the tetrameric cations; the SO_3^- halves of an $S_2O_6^{2-}$ anion show the usual staggered configuration. Average S–O and S–S bond lengths are 1.47 and 2.11 Å, respectively. The water molecules of crystallization exhibit considerable mobility in the crystal at room temperature, as documented by rather large isotropic thermal parameters (supplementary material) for the oxygen atoms.

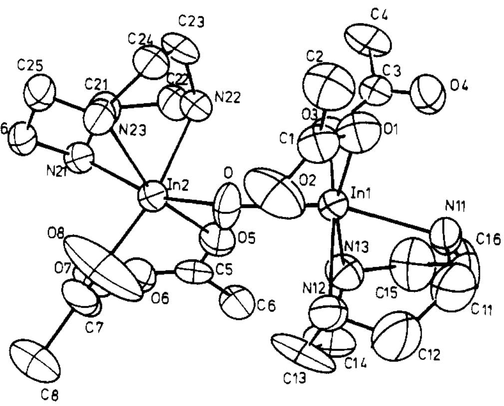

Figure 2. Perspective view of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]$ and atomic labeling scheme.

Description of the Structure of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot 2NaClO_4$. Crystals of $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot 2NaClO_4$ consist of the dimeric, neutral species $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]$ and of sodium cations and perchlorate anions. Figure 2 shows a perspective view and the atomic labeling scheme of the dimer. Two $LIn(CH_3CO_2)_2^+$ moieties are linked by an oxo bridge. The average In–O distance of this bridge is 2.114 Å, which compares well with values found for the cubic[22] and rhombohedral[16] modifications of In_2O_3, where indium(III) is six-coordinate (octahedron). The In–O bond length is slightly shorter than the In–O distance in the hydroxo-bridged tetramer. The In–O–In bond angle is 142.5 (2)°—a nonlinear μ-oxo bridge.

Both indium(III) centers are coordinated to a tridentate macrocycle, respectively; the average In–N bond length is 2.297 Å, in good agreement with that in $[L_4In_4(\mu\text{-}OH)_6]^{4+}$.

In addition, each indium(III) is coordinated to two acetate groups, one of which is clearly monodentate, whereas the second may be considered bidentate with one short In–O bond distance of 2.14 Å and a rather long In–O bond of 2.87 Å. Bidentate carboxylato ligands have been identified in a number of other indium(III) complexes,[17,18,23,24] but in these cases, both In–O bonds are more or less equivalent and the In–O bond lengths range from 2.25 to 2.38 Å. Recently, the structure of an (acetato)(porphyrinato)indium(III) complex has been determined, which also contains an unsymmetrically bound bidentate acetato ligand (In–O = 2.14 and 2.60 (1) Å).[25]

Thus, both indium(III) centers attain the coordination number 7.

The sodium cations in $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot 2NaClO_4$ are surrounded by six oxygen atoms in a distorted octahedral arrangement: O1 and O4 of the acetate ligands are bound to Na1; O6 and O7 of the carboxylate groups are bound to Na2; one oxygen atom of each ClO_4^- is also coordinated to a sodium cation (O13 to Na1 and O22 to Na2). The Na–O distances range from 2.40 to 2.79 Å.

Concluding Remarks

Tuck et al. have recently described a series of complexes of In(I) and In(III) containing the tetradentate N-donor macrocycle 1,4,8,11-tetraazacyclotetradecane (cyclam).[26] The reaction of InX_3 (X = Cl, Br, I) in nonaqueous solvents with the ligand yielded products of composition $[InX_2L][InX_4]$. We have shown in this study that the smaller tridentate N-donor macrocycles bind strongly to In(III) even in aqueous solution, forming 1:1 complexes. Hydrolysis of $LInBr_3$ in alkaline solution yielded the first examples

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of a well-characterized μ-hydroxo- and μ-oxo-bridged indium(III) complex.

Safety Note. Perchlorate salts containing organic ligands are potentially explosive, especially when heated. Only small quantities should be prepared.

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Registry No. $LInCl_3$, 101652-41-9; $L'InCl_3$, 101652-42-0; $L''InCl_3$, 101652-43-1; $LInBr_3$, 101652-44-2; $[L_2In](ClO_4)_3$, 101652-46-4; $[L_4In_4(\mu\text{-}OH)_6](ClO_4)_6$, 101670-87-5; $[L_4In_4(\mu\text{-}OH)_6](S_2O_6)_3 \cdot 4H_2O$, 101670-89-7; $[L_4In_4(\mu\text{-}OH)_6]I_6$, 101652-47-5; $[L_4In_4(\mu\text{-}OH)_6](PF_6)_6$, 101652-49-7; $[(LIn(CH_3CO_2)_2)_2O]\cdot 2NaClO_4$, 101652-51-1; $[L_2In_2(SH)_3]Br_3$, 101670-90-0; $[L_2In_2(SH)_3](ClO_4)_3$, 101652-53-3.

Supplementary Material Available: Tables containing thermal parameters (isotropic and anisotropic) and calculated positional parameters of hydrogen atoms for both structures (6 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (66 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, FRG, and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, FRG

Syntheses of $[LRe(CO)_3]^+$ and $[LRe(NO)(CO)_2]^{2+}$ and Their Oxidative Decarbonylation Product $[LReO_3]^+$. Crystal Structure of $[LReO_3]Cl$ (L = 1,4,7-Triazacyclononane)

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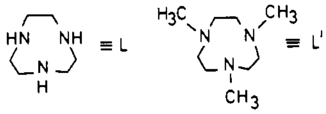
The reaction of $Re(CO)_5Br$ with 1,4,7-triazacyclononane ($C_6H_{15}N_3$; L) in dimethylformamide afforded air-stable, colorless $[LRe(CO)_3]Br$, which reacted with $NOBF_4$ to give yellow $[LRe(NO)(CO)_2](BF_4)_2$. Oxidative decarbonylation of $[LRe(CO)_3]Br$ with nitric acid yielded colorless $[LReO_3]ReO_4$, whereas $[LRe(NO)(CO)_2](BF_4)_2$ reacted in 35% H_2O_2 to give $[LReO_3]BF_4$. The structure of colorless $[LReO_3]Cl$ has been determined. It crystallized in the hexagonal system, space group $P6_3$, with $a = 7.792$ (1) Å, $c = 10.857$ (2) Å, and $Z = 2$. The structure was refined to a final R value of 0.0305 for 1092 unique reflections. The coordination sphere at the Re(VII) centers consists of three facially coordinated nitrogen atoms of the tridentate amine and three terminal oxo groups. The Re–O bond distance of 1.756 (5) Å is very short, indicating considerable multiple-bond character. The O–Re–O angles are obtuse (102.7 (4)°).

Introduction

We have recently shown in a series of papers[2-7] that the macrocyclic ligands 1,4,7-triazacyclononane (L) and 1,4,7-trimethyl-1,4,7-triazacyclononane (L′) coordinate strongly to a



variety of monomeric transition-metal carbonyl complexes, affording $[LM(CO)_3]^{n+}$ and $L'M(CO)_3$ species ($n = 0$, M = Cr,[2] Mo,[2,5-7] W;[2,3] $n = 1$, M = Mn[3]) in excellent yields. These complexes were used to synthesize complexes containing the LM^{n+} moiety, the metal centers in higher oxidation states, via oxidative decarbonylation reactions, e.g. eq 1 and 2.

$$LM(CO)_3 + 1.5X_2 \rightarrow LMX_3 + 3CO \qquad (1)$$

X = Cl, Br; M = Cr, Mo, W

$$2L'M(CO)_3 \xrightarrow{HNO_3} [L'_2M_2O_5]^{2+} \qquad (2)$$

M = Mo, W

We have now extended these investigations to rhenium chemistry using $Re(CO)_5Br$ as starting material. We here report the oxidative decarbonylation reactions of $[LRe(CO)_3]^+$ and $[LRe(NO)(CO)_2]^{2+}$ yielding the monomeric cation $[LReO_3]^+$. The analogous syntheses and chemistry of the organometallic species $(\eta^5\text{-}Me_5C_5)ReO_3$ have recently been developed by Herrmann and co-workers.[8,9]

Experimental Section

The ligand 1,4,7-triazacyclononane (L) was prepared by procedures described in the literature.[10] Infrared spectra were recorded on a Beckman Acculab 10 spectrophotometer as KBr pellets.

Preparation of Complexes. $[LRe(CO)_3]Br$. To an argon-scrubbed solution of $Re(CO)_5Br$[11] (2.4 g, 5 mmol) in dimethylformamide (DMF) (10 mL) was added 1,4,7-triazacyclononane (0.8 g, 5 mmol). This solution was stirred for 24 h at room temperature. A colorless precipitate was filtered off, washed with ether, and air-dried. Addition of diethyl ether to the mother liquor initiated the precipitation of more product (yield ~65% based on Re). This material was recrystallized from a minimum amount of acetone/H_2O or acetonitrile/H_2O mixtures (2:1), yielding colorless crystals, which are air-stable in solution and in the solid state.

Anal. Calcd for $C_9H_{15}N_3O_3BrRe$: C, 22.55; H, 3.18; N, 8.77; Br, 16.67. Found: C, 23.1; H, 3.3; N, 9.0; Br, 16.4.

$[LRe(NO)(CO)_2](BF_4)_2$. A solution of $[LRe(CO)_3]Br$ (0.48 g, 1 mmol) in acetonitrile (20 mL) and $NOBF_4$ (0.36 g, 3 mmol) was refluxed for 60 min. The solution was allowed to stand at room temperature for 12 h, after which time yellow crystals were filtered off, washed with acetone and ether, and air-dried (yield 81%). The product was recrystallized from hot acetonitrile.

Anal. Calcd for $C_8H_{15}N_4O_3Re(BF_4)_2$: C, 16.71; H, 2.63; N, 9.74. Found: C, 17.0; H, 2.7; N, 9.7.

$[LReO_3]ReO_4$. A solution of $[LRe(CO)_3]Br$ (0.48 g, 1 mmol) in 5 M nitric acid (10 mL) was refluxed for 24 h, after which time the volume of the solution was reduced (~5 mL) on a rotary evaporator. A microcrystalline, colorless solid precipitated at room temperature, which was filtered off, washed with ether, and air-dried. The material was re-

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