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Polydentate Ligand Chemistry of Group 13 Metals: Effects of the Size and Donor Selectivity of Metal Ions on the Structures and Properties of Aluminum, Gallium, and Indium Complexes with Potentially Heptadentate (N_4O_3) Amine Phenol Ligands

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The aluminum, gallium and indium complexes of potentially heptadentate (N_4O_3) tripodal amine phenol ligands (H_3L1 = tris(2′-hydroxybenzylaminoethyl)amine, H_3L2 = tris(5′-chloro-2′-hydroxybenzylaminoethyl)amine, and H_3L3 = tris(5′-bromo-2′-hydroxybenzylaminoethyl)amine) have been prepared and characterized. The spectral (IR, FAB-MS, and ^1H NMR) properties of these complexes are reported. The reaction of Al^{3+} or Ga^{3+} with N_4O_3 amine phenols in presence of 3 equiv of a base (acetate or hydroxide) afforded cationic complexes, [M(HL)]X (M = Al, L = L1, L2, L3, X = ClO_4^-; M = Ga, L = L1, L3, X = NO_3^-, Cl^-), while neutral In complexes [In(L)] (L = L1, L2, L3) were obtained from similar reactions. The molecular structures of $[Al(HL2)]ClO_4\cdot 2CH_3OH$, $[Ga(HL3)]Cl\cdot CHCl_3$, and $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$ were determined by X-ray methods. Crystals of $[Al(HL2)](ClO_4)\cdot 2CH_3OH$ are triclinic, $P\bar{1}$, $a = 9.2567$ (9) Å, $b = 11.6025$ (9) Å, $c = 8.9471$ (6) Å, $\alpha = 109.251$ (6)°, $\beta = 96.952$ (8)°, $\gamma = 71.452$ (7)°, $V = 859.9$ (1) Å^3, and $Z = 1$; those of $[Ga(HL3)]Cl\cdot CHCl_3$ are monoclinic, $P2_1/n$, $a = 11.390$ (3) Å, $b = 14.306$ (2) Å, $c = 21.700$ (2) Å, $\beta = 92.29$ (1)°, $V = 3533$ (1) Å^3, and $Z = 4$; and those of $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$ are tetragonal, $I4_1/a$, $a = 18.974$ (2) Å, $c = 39.255$ (3) Å, $V = 14133$ (2) Å^3, and $Z = 16$. The three structures were refined to $R = 0.037$, 0.052, and 0.043 and $R_w = 0.045$, 0.061, and 0.053 for 3471, 4979, and 4903 observed reflections with $I \geq 3\sigma(I)$, for the Al, Ga, and In complexes, respectively. The Al atom in $[Al(HL2)]ClO_4\cdot 2CH_3OH$ is coordinated by an N_3O_3 donor set from the N_4O_3 amine phenol ligand in a distorted octahedral coordination geometry with one (N(4)) of the three secondary amine N atoms being protonated and uncoordinated. The Ga atom in $[Ga(HL3)]Cl\cdot CHCl_3$ is bonded by six (N_4O_2) donor atoms of the N_4O_3 amine phenol ligand in a distorted octahedral geometry with one phenol oxygen being protonated and uncoordinated. In $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$, all seven ($N_4O_3$) donors coordinate to the In atom in a monocapped distorted octahedral arrangement. The structural differences among these complexes are discussed in terms of the donor atom selectivity and the size of the metal ions. Variable-temperature ^1H NMR spectral data revealed rigid solution structures for both the aluminum and gallium complexes. These complexes remained very rigid at solution temperatures higher than 120 °C. Stereochemical changes in the indium complexes were observed at room temperature, and they undergo an intramolecular dissociative inversion at the coordinated N atoms at elevated temperatures. The ^1H NMR spectral properties of aluminum, gallium, and indium complexes are discussed in relation to their structural differences.

Introduction

We are interested in the polydentate coordination chemistry of aluminum, gallium, and indium as it may pertain to the roles played by group 13 metal ions in the genesis and diagnosis of disease. We have been studying their tris(ligand) complexes containing bidentate monobasic ligands.[2–6] Unique combinations of properties (water solubility, hydrolytic stability, and lipophilicity) have led to the wide use of tris(maltolato)aluminum in the study of Al neurotoxicity[7] and the potential application of a ^{67}Ga complex for heart imaging.[8]

The extensive complicated hydrolysis chemistries of aluminum, gallium, and indium have limited most quantitative studies of solution reactions of these elements to acidic media,[9,10] leaving less well developed the study of aluminum, gallium, and indium complexes in aqueous solution, especially at neutral pH. Recent research has been directed toward the design of polydentate ligand systems which have the potential to form highly stable complexes with group 13 metal ions, either for the treatment of Al overload or for the development of Ga and In radiopharmaceuticals.[11–20]

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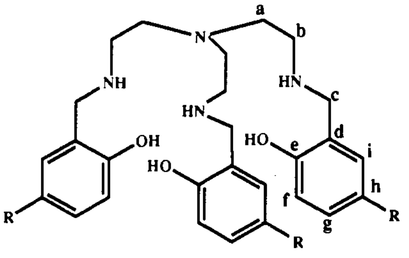
Polydentate ligands with intrinsically three-dimensional cavities are of particular interest because of the high stability of their metal complexes, the substantial selectivity in their binding by enforcing a specific spatial arrangement of donor atoms or by introducing different donor atoms, and their preorganized frameworks. Recently, we reported three potentially heptadentate (N_4O_3) tripodal amine phenols (H_3L1, H_3L2, and H_3L3), in which three chelating arms are bridged by a tertiary nitrogen atom.[21] These ligands form very stable mononuclear $[Ln(H_3L)(NO_3)_3]$ and dinuclear $[Ln(L)]_2$ lanthanide complexes depending on the conditions of preparation. A structural study revealed the first example, $[Gd(L1)]_2{\cdot}2CHCl_3$, of a homodinuclear lanthanide complex, $[Ln(L)]_2$, with a heptadentate (N_4O_3 amine phenol) ligand only. Furthering this study, we now present the synthesis, structures and characterization of aluminum, gallium, and indium complexes of these three amine phenols and the subtle structural differences in coordinating properties depending on the metal ion involved.



H_3L1, R=H
H_3L2, R=Cl
H_3L3, R=Br

Experimental Section

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with care and only in small amounts.

Materials. Hydrated metal salts were obtained from Aldrich or Alfa and were used without further purification. The amine phenols, tris(2′-hydroxybenzylaminoethyl)amine (H_3L1), tris(5′-chloro-2′-hydroxybenzylaminoethyl)amine (H_3L2), and tris(5′-bromo-2′-hydroxybenzylaminoethyl)amine (H_3L3), were prepared according to previously reported methods.[21]

Instrumentation. NMR spectra (200 Mz and 300 Mz) were recorded on Bruker AC-200E (^1H–^1H COSY and APT ^{13}C NMR) and Varian XL 300 (VT ^1H NMR) spectrometers, respectively, with δ relative to TMS. Mass spectra were obtained with an AEI MS-9 instrument (fast atom bombardment ionization, FAB). Infrared spectra were recorded as KBr disks in the range 4000–400 cm^{-1} on a Perkin-Elmer PE783 spectrophotometer and were referenced to polystyrene. Melting points were measured on a Mel-Temp apparatus and are uncorrected. Analyses for C, H, and N were performed by Mr. Peter Borda in this department.

Tris(5′-bromo-2′-hydroxybenzylaminoethyl)amine Trihydrochloride Monohydrate ($H_3L3{\cdot}3HCl{\cdot}H_2O$). The ligand H_3L3 as its trihydrochloride salt was prepared according to the previously reported method (for the free base) with some modification.[21] To a suspension of the Schiff base H_3(Brsaltren) (3.98 g, 5.0 mmol) in hot methanol (200 mL) was added KBH_4 (1.06 g, 20 mmol) in small portions over 30 min. After addition the reaction mixture was refluxed for an hour. The solvent was removed on a rotary evaporator, and to the residue was added NH_4Cl (10 g) in water (100 mL). The mixture was extracted with chloroform (3 × 150 mL). The organic fractions were combined and taken to dryness to afford a white solid. The solid was dried under vacuum overnight. Yield was 3.2 g (79%), mp 150–153 °C. Anal. Calcd (found) for $C_{27}H_{38}Br_3Cl_3N_4O_4$: C, 39.13 (38.99); H, 4.62 (4.73); N, 6.76 (6.73). Mass spectrum (FAB): $m/z = 703$ (M + 1, $[C_{27}H_{34}Br_3N_4O_3]^+$). IR (cm^{-1}, KBr disk): 3600–2000 (br, ν_{O-H} and ν_{N-H}); 1605 and 1590 (s, δ_{N-H}). NMR (DMSO-d_6, chemical shift δ relative to TMS, assignments based on those for the free base[21]): ^{13}C, 156.1 (C_e), 133.8 (C_i), 132.6 (C_g), 121.4 (C_d), 117.8 (C_f), 109.8 (C_h), 56.1 (C_b), 50.1 (C_c), 45.1 (C_a); ^1H, 7.65 (s, 3H, H_i), 7.36 (d, 3H, ^3J = 6.7 Hz, H_g), 7.25 (bs, OH and NH), 6.98 (d, 3H, ^3J = 6.8 Hz, H_f), 4.14 (s, 6H, H_c), 3.00 (bs, 6H, H_b), 2.70 (bs, 6H, H_a).

$[Al(HL1)]ClO_4{\cdot}1.5H_2O$. To a solution of $Al(ClO_4)_3{\cdot}9H_2O$ (487 mg, 1.0 mmol) in methanol (20 mL) was added H_3L1 (480 mg, 1.03 mmol) in chloroform (10 mL). After addition of $NaOAc{\cdot}3H_2O$ (420 mg, 3.0 mmol) in methanol (10 mL), the mixture was filtered immediately and the filtrate was kept standing at room temperature until pink crystals were deposited. These were collected by filtration, washed with water (3 mL) and ethanol, and dried in air. Yield was 350 mg (57%). Anal. Calcd (found) for $C_{27}H_{37}AlClN_4O_{8.5}$: C, 52.64 (52.97); H, 6.05 (5.77); N, 9.09 (8.78). Mass spectrum (FAB): $m/z = 489$ (M, $[C_{27}H_{34}AlN_4O_3]^+$). IR (cm^{-1}, KBr disk): 3650–2300 (br, ν_{O-H}); 3140 (s, ν_{N-H}); 1600 and 1570 (s, δ_{N-H}); 1120–1050 (bs, $\nu_{ClO_4^-}$); 625 (s, $\nu_{ClO_4^-}$).

$[Al(HL2)]ClO_4{\cdot}2CH_3OH$. The complex was prepared similarly using $Al(ClO_4)_3{\cdot}9H_2O$ (244 mg, 0.5 mmol), H_3L2 (420 mg, 0.53 mmol), and $NaOAc{\cdot}3H_2O$ (280 mg, 2.0 mmol). Pink crystals suitable for X-ray diffraction study were isolated from the reaction mixture. Yield was 260 mg (72%). Anal. Calcd (found) for $C_{29}H_{39}AlCl_4N_4O_9$: C, 46.02 (45.68); H, 5.20 (5.10); N, 7.41 (7.25). Mass spectrum (FAB): $m/z = 590$ (M, $[C_{27}H_{31}AlCl_3N_4O_3]^+$). IR (cm^{-1}, KBr disk): 3400 (br, ν_{O-H}); 3240, 3220 (m, ν_{N-H}); 1596 (s, δ_{N-H}); 1120–1050 (bs, $\nu_{ClO_4^-}$); 625 (s, $\nu_{ClO_4^-}$).

$[Al(HL3)]ClO_4{\cdot}2.5H_2O$. The complex was prepared similarly to $[Al(HL1)]ClO_4{\cdot}1.5H_2O$ using $Al(ClO_4)_3{\cdot}9H_2O$ (244 mg, 0.5 mmol), H_3L3 (350 mg, 0.5 mmol), and $NaOAc{\cdot}3H_2O$ (280 mg, 2.0 mmol). Pink microcrystals were isolated. Yield was 292 mg (66%). Anal. Calcd (found) for $C_{27}H_{36}AlBr_3ClN_4O_{9.5}$: C, 37.24 (37.31); H, 4.17 (4.00); N, 6.43 (6.40). Mass spectrum (FAB): $m/z = 725$ (M, $[C_{27}H_{31}AlBr_3N_4O_3]^+$. IR (cm^{-1}, KBr disk): 3400 (br, ν_{O-H}); 3240, 3220 (m, ν_{N-H}); 1590 (s, δ_{N-H}) 1130–1050 (bs, $\nu_{ClO_4^-}$); 625 (s, $\nu_{ClO_4^-}$).

$[Ga(HL1)](NO_3)$. To a solution of $Ga(NO_3)_3{\cdot}9H_2O$ (209 mg, 0.5 mmol) in methanol (20 mL) was added H_3L1 (240 mg, 0.52 mmol) in the same solvent (10 mL). After addition of $NaOAc{\cdot}3H_2O$ (280 mg, 2.0 mmol) in methanol (10 mL), the mixture was filtered immediately. Slow evaporation of solvent at room temperature afforded pink microcrystals, which were collected by filtration, washed with cold ethanol and diethyl ether, and dried in air. Yield was 200 mg (67%). Anal. Calcd (found) for $C_{27}H_{34}GaN_5O_6$: C, 54.57 (54.45); H, 5.77 (5.52); N, 11.78 (11.89). Mass spectrum (FAB): $m/z = 531$ (M, $[C_{27}H_{34}GaN_4O_3]^+$). IR (cm^{-1}, KBr disk): 3650–2300 (br, ν_{O-H}); 3140 (s, ν_{N-H}); 1600 and 1570 (s, δ_{N-H}); 1380 and 1280 (vs, $\nu_{NO_3^-}$). The product prepared from the reaction of $Ga(NO_3)_3{\cdot}9H_2O$ with H_3L1 in the presence of 3 equiv of sodium hydroxide was shown by IR, NMR, FAB-MS, and elemental analysis to be identical to that obtained by the method above.

$[Ga(HL3)]Cl{\cdot}CHCl_3$. To a solution of $Ga(NO_3)_3{\cdot}9H_2O$ (209 mg, 0.5 mmol) in methanol (20 mL) was added $H_3L3{\cdot}3HCl{\cdot}H_2O$ (415 mg, 0.5 mmol) in a mixture of chloroform (20 mL) and methanol (10 mL). Upon addition of 2 M NaOH solution (3 mL, 6.0 mmol) dropwise, the cloudy solution became clear, and it was filtered. The filtrate was kept standing at room temperature; slow evaporation afforded pink crystals suitable for X-ray diffraction. These were collected by filtration, washed with cold ethanol and diethyl ether, and dried in air. Yield was 340 mg (45%). Anal. Calcd (found) for $C_{28}H_{32}GaBr_3Cl_4N_4O_3$: C, 36.40 (36.28); H, 3.49 (3.56); N, 6.06 (6.38). Mass spectrum (FAB): $m/z = 769$ (M, $[C_{27}H_{31}GaBr_3N_4O_3]^+$). IR (cm^{-1}, KBr disk): 3420 (br, ν_{O-H}); 3200 (bm, ν_{N-H}); 1589 (m, δ_{N-H}).

$[In(L1)]{\cdot}0.5H_2O$. A procedure similar to that for $[Ga(HL1)](NO_3)$ was employed using $In(NO_3)_3{\cdot}5H_2O$ (195 mg, 0.5 mmol), H_3L1 (240 mg, 0.52 mmol), and $NaOAc{\cdot}3H_2O$. Colorless microcrystals were isolated. Yield was 280 mg (86%). Anal. Calcd (found) for $C_{27}H_{34}InN_4O_{3.5}$: C, 55.40 (55.47); H, 5.85 (5.71); N, 9.57 (9.59). Mass spectrum (FAB): $m/z = 576$ (M, $[C_{27}H_{33}InN_4O_3]^+$). IR (cm^{-1}, KBr disk): 3600–3000 (bm, ν_{O-H}); 3240 (m, ν_{N-H}); 1595 and 1565 (s or m, δ_{N-H}).

$Na[In(L1)](NO_3)(H_2O)(ROH){\cdot}3H_2O$ ($R = CH_3, C_2H_5$). To a solution of $In(NO_3)_3{\cdot}5H_2O$ (391 mg, 1.0 mmol) in methanol (30 mL) was added H_3L1 (480 mg, 1.05 mmol) in chloroform (10 mL) followed by 1.5 mL of a 2 M NaOH solution (3.0 mmol). The mixture was filtered immediately, and the filtrate was left standing at room temperature until colorless crystals were deposited. They were isolated by filtration, washed with ethanol and diethyl ether, and dried in air. Yield was 395 mg (57% based on In). These crystals became opaque and amorphous after separation from the mother liquor. Anal. Calcd (found) for $C_{28}H_{45}InN_5NaO_{11}$ ($R = CH_3$): C, 43.93 (43.86); H, 5.93 (5.90); N, 9.15 (9.13). The filtrate above was kept in a flask overnight to give colorless crystals. They were separated by filtration, washed with ethanol and diethyl ether, and dried in air, suitable crystals were selected for an X-ray diffraction

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Table I. Selected Crystallographic Data for $[Al(HL2)]ClO_4 \cdot 2CH_3OH$, $[Ga(HL3)]Cl \cdot CHCl_3$ and $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$

	$[Al(HL2)]ClO_4 \cdot 2CH_3OH$	$[Ga(HL3)]Cl \cdot CHCl_3$	$Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$
formula	$C_{29}H_{39}AlCl_4N_4O_9$	$C_{28}H_{32}Br_3Cl_4GaN_4O_3$	$C_{29}H_{41}InN_5NaO_8 \cdot 2.65H_2O$
fw	756.44	923.83	773.22
cryst syst	triclinic	monoclinic	tetragonal
space group	$P1$	$P2_1/n$	$I4_1/a$
a, Å	9.2567 (9)	11.390 (3)	18.974 (2)
b, Å	11.6025 (9)	14.306 (2)	18.974 (2)
c, Å	8.9471 (6)	21.700 (2)	39.255 (3)
α, deg	109.251 (6)	90	90
β, deg	96.952 (8)	92.29 (1)	90
γ, deg	71.452 (7)	90	90
V	859.9 (1)	3533 (1)	14133 (2)
Z	1	4	16
ρ_c, g/cm^3	1.461	1.737	1.453
T, °C	21	21	21
radiation (λ, Å)	Cu (1.541 78)	Cu (1.541 78)	Cu (1.541 78)
μ(Cu Kα), cm^{-1}	39.22	82.38	60.83
transm factors	0.86–1.00	0.37–1.00	0.54–1.00
R	0.037	0.052	0.043
R_w	0.045	0.061	0.053

study. Yield was 150 mg (22% based on In). Anal. Calcd (found) for $C_{29}H_{47}InN_5NaO_{11}$ ($R = C_2H_5$): C, 44.68 (44.65); H, 6.08 (5.79); N, 8.98 (8.84). IR (cm^{-1}, KBr disk): 3600–3000 (bs, ν_{O-H}); 3240 (m, ν_{N-H}); 1595 and 1565 (s or m, δ_{N-H}); 1380 and 1280 (vs, $\nu_{NO_3^-}$).

$In(L2)] \cdot 3.5H_2O$. The complex was prepared similarly to $[Ga(HL3)]Cl \cdot CHCl_3$ using $In(NO_3)_3 \cdot 5H_2O$ (195 mg, 0.5 mmol) in methanol (20 mL), H_3L2 (290 mg, 0.5 mml) in dichloromethane (20 mL), and 1.0 mL of a 2 M NaOH solution (2.0 mmol). White crystals were obtained. Yield was 255 mg (69%). Anal. Calcd (found) for $C_{27}H_{37}Cl_3InN_4O_{6.5}$: C, 43.66 (43.61); H, 5.02 (5.05); N, 7.54 (7.41). Mass spectrum (FAB): $m/z = 679$ ($[C_{27}H_{30}Cl_3InN_4O_3]^+$). IR (cm^{-1}, KBr disk): 3600–2700 (bs, ν_{N-H}); 3200 (br, ν_{N-H}); 1590 and 1560 (s or w, δ_{N-H}).

$[In(L3)] \cdot 2H_2O$. The complex was obtained as a white crystalline solid in a manner similar to the preparation of $[Ga(HL3)]Cl \cdot CHCl_3$ using $In(NO_3)_3 \cdot 5H_2O$ (195 mg, 0.5 mmol) in methanol (20 mL), $H_3L3 \cdot 1.5H_2O$ (365 mg, 0.5 mmol) in $CHCl_3$ (10 mL) and 2M NaOH (1.0 mL) solution (2.0 mmol). Yield was 350 mg (82%). Anal. Calcd (found) for $C_{27}H_{34}Br_3InN_4O_5$: C, 38.19 (38.19); H, 4.04 (4.15); N, 6.30 (6.23). Mass spectrum (FAB): $m/z = 816$ (M, $[C_{27}H_{30}Br_3InN_4O_3]^+$). IR (cm^{-1}, KBr disk); 3600–3000 (br, ν_{O-H}); 3240 (m, ν_{N-H}); 1590 and 1562 (s or m, δ_{N-H}).

X-ray Crystallographic Analyses. Selected crystallographic data for the three compounds appear in Table I. The final unit cell parameters were obtained by least-squares methods on the setting angles for 25 reflections with $2\theta = 55.7$–79.3° for $[Al(HL2)](ClO_4) \cdot 2CH_3OH$, 79.3–99.8° for $[Ga(HL3)]Cl \cdot CHCl_3$, and 92.2–97.7° for $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$. The intensities of three standard reflections, measured every 200 or 250 reflections throughout the data collections, decayed uniformly by 4.4% for $[Ga(HL3)]Cl \cdot CHCl_3$, and were essentially constant for $[Al(HL2)](ClO_4) \cdot 2CH_3OH$ and $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$. The data were processed and corrected for Lorentz and polarization effects, decay (for $[Ga(HL3)]Cl \cdot CHCl_3$), and absorption (empirical, based on azimuthal scans for three reflections).[22]

The structure of the aluminum complex $[Al(HL2)](ClO_4) \cdot 2CH_3OH$ was solved by direct methods and those of the gallium and indium complexes were solved by conventional heavy-atom methods, the coordinates of the heavy atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The structure analysis of $[Al(HL2)](ClO_4) \cdot 2CH_3OH$ was initiated in the noncentrosymmetric space group $P1$, based on E statistics and the fact that there is only one formula unit in the unit cell; this choice was confirmed by the subsequent successful solution and refinement of the structure. The asymmetric unit of $[Al(HL2)](ClO_4) \cdot 2CH_3OH$ (the entire unit cell) contains two solvate molecules of methanol in addition to the complex cation and the perchlorate anion. The asymmetric unit of $[Ga(HL3)]Cl \cdot CHCl_3$ contains the complex cation, a chloride anion, and one molecule of chloroform. The Cl atoms of the chloroform solvate in $[Ga(HL3)]Cl \cdot CHCl_3$ are disordered over two sets of positions related by a rotation about the C–H bond. The site occupancy for Cl(4) was refined while constrained to be equal to those of the other two high-occupancy Cl atoms (Cl(2) and Cl(3)). The site occupancy factors for the minor component Cl atoms (Cl(2B), Cl(3B), and Cl(4B)) were constrained to be one minus that of the major component. In the asymmetric unit of the indium complex $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$ there are 2.65 molecules of water disordered over seven different sites. The site occupancy factor for O(15), the highest-occupancy site, was successfully refined while occupancy factors for the remaining sites could not be refined and were adjusted to give approximately equal thermal parameters. The carbon atoms of the ethanol ligand were also found to be disordered, the α- and β-carbon atoms being refined as 2-fold and 3-fold disordered, respectively. As for the water molecules, attempted simultaneous refinement of the site occupancy factors and thermal parameters was not successful. The occupancy factors were once again adjusted to result in approximately equal thermal parameters. The structure of $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$ contains cavities occupied by the disordered water molecules. The portions of the complex molecule that project into these cavities (the nitrate, ethanol, and water ligands of Na) all display, in addition to the disorder of the ethanol ligand, a high degree of thermal motion. This aspect of the structure is entirely consistent with the rapid deterioration of the crystals of this material when removed from the mother liquor.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $[Al(HL2)]ClO_4 \cdot 2CH_3OH$

Bond Lengths			
Al(1)–O(1)	1.838 (3)	Al(1)–N(1)	2.207 (3)
Al(1)–O(2)	1.824 (3)	Al(1)–N(2)	2.095 (4)
Al(1)–O(3)	1.819 (3)	Al(1)–N(3)	2.056 (3)
Bond Angles			
O(1)–Al(1)–O(2)	96.1 (1)	O(2)–Al(1)–N(3)	90.8 (1)
O(1)–Al(1)–O(3)	90.3 (1)	O(3)–Al(1)–N(1)	89.3 (1)
O(1)–Al(1)–N(1)	91.2 (1)	O(3)–Al(1)–N(2)	168.6 (1)
O(1)–Al(1)–N(2)	88.3 (1)	O(3)–Al(1)–N(3)	88.3 (1)
O(1)–Al(1)–N(3)	173.2 (1)	N(1)–Al(1)–N(2)	79.4 (1)
O(2)–Al(1)–O(3)	110.1 (1)	N(1)–Al(1)–N(3)	82.1 (1)
O(2)–Al(1)–N(1)	167.3 (1)	N(2)–Al(1)–N(3)	91.7 (1)
O(2)–Al(1)–N(2)	90.3 (1)		

All non-hydrogen atoms with the exception of the low-occupancy Cl atoms in $[Ga(HL3)]Cl \cdot CHCl_3$, the disordered ethanol carbon atoms in $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$, and the water oxygen atoms having site occupancies of less than 0.5 in $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$ were refined with anisotropic thermal parameters. The hydrogen atoms in $[Al(HL2)](ClO_4) \cdot 2CH_3OH$ and $[Ga(HL3)]Cl \cdot CHCl_3$, and those associated with the heptadentate ligand in $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$ were fixed in idealized positions (based on difference map positions where appropriate, $d_{(C,N,O)-H} = 0.98$ Å, $B_H = 1.2B_{\text{bonded atom}}$). Hydrogen atoms associated with the disordered ethanol ligand and disordered water molecules in $Na[In(L1)][NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$ were not included in the model. Secondary extinction corrections were applied in all three cases, the final values of the extinction coefficient being 4.76×10^{-6}, 5.72×10^{-8}, and 6.16×10^{-8}, respectively for $[Al(HL2)](ClO_4) \cdot 2CH_3OH$, $[Ga(HL3)]Cl \cdot CHCl_3$, and $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH) \cdot 2.65H_2O$. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 23. For the noncentrosymmetric structure $[Al(HL2)](ClO_4) \cdot 2CH_3OH$, a parallel refinement of the mirror-image structure was carried out in order to determine the absolute configuration (for the particular crystal employed for data collection). The residuals for the mirror-image structure were significantly higher, the R and R_w ratios being 1.176 and 1.179, respectively.

Selected bond lengths and bond angles for the three structures appear in Tables II–IV. Complete tables of crystallographic data, bond distances, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and final atomic coordinates and equivalent isotropic thermal parameters for the

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(22) TEXSAN/TEXRAY structure analysis package, which includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(23) *International Tables for X-Ray Crystallograhy*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in [Ga(HL3)]Cl·$CHCl_3$

Bond Lengths			
Ga(1)–O(1)	1.897 (4)	Ga(1)–N(2)	2.099 (5)
Ga(1)–O(3)	1.906 (4)	Ga(1)–N(3)	2.115 (4)
Ga(1)–N(1)	2.147 (5)	Ga(1)–N(4)	2.090 (4)
Bond Angles			
O(1)–Ga(1)–O(3)	95.5 (2)	O(3)–Ga(1)–N(4)	92.0 (2)
O(1)–Ga(1)–N(1)	91.7 (2)	N(1)–Ga(1)–N(2)	81.7 (2)
O(1)–Ga(1)–N(2)	89.1 (2)	N(1)–Ga(1)–N(3)	82.8 (2)
O(1)–Ga(1)–N(3)	80.0 (2)	N(1)–Ga(1)–N(4)	80.9 (2)
O(1)–Ga(1)–N(4)	171.3 (2)	N(2)–Ga(1)–N(3)	160.7 (2)
O(3)–Ga(1)–N(1)	172.7 (2)	N(2)–Ga(1)–N(4)	94.3 (2)
O(3)–Ga(1)–N(2)	97.3 (2)	N(3)–Ga(1)–N(4)	94.4 (2)
O(3)–Ga(1)–N(3)	99.5 (2)		

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)·2.65H_2O

Bond Lengths			
In(1)–O(1)	2.177 (3)	In(1)–N(1)	2.752 (4)
In(1)–O(2)	2.174 (3)	In(1)–N(2)	2.333 (4)
In(1)–O(3)	2.155 (4)	In(1)–N(3)	2.324 (4)
In(1)–N(4)	2.333 (4)		
Na(1)–O(3)	2.449 (5)	Na(1)–O(1)	2.434 (5)
Na(1)–O(5)	2.542 (9)	Na(1)–O(4)	2.43 (1)
Na(1)–O(8)	2.419 (8)	Na(1)–O(7)	2.415 (8)
Bond Angles			
O(1)–In(1)–O(2)	85.3 (1)	O(3)–In(1)–N(1)	129.7 (1)
O(1)–In(1)–O(3)	82.3 (1)	O(3)–In(1)–N(2)	82.0 (1)
O(1)–In(1)–N(1)	130.7 (1)	O(3)–In(1)–N(3)	162.2 (2)
O(1)–In(1)–N(2)	84.7 (1)	O(3)–In(1)–N(4)	84.8 (2)
O(1)–In(1)–N(3)	82.2 (1)	N(1)–In(1)–N(2)	67.8 (1)
O(1)–In(1)–N(4)	161.5 (1)	N(1)–In(1)–N(3)	67.8 (1)
O(2)–In(1)–O(3)	85.4 (1)	N(1)–In(1)–N(4)	67.7 (1)
O(2)–In(1)–N(1)	127.2 (1)	N(2)–In(1)–N(3)	105.3 (1)
O(2)–In(1)–N(2)	164.9 (2)	N(2)–In(1)–N(4)	106.5 (1)
O(2)–In(1)–N(3)	84.6 (2)	N(3)–In(1)–N(4)	107.9 (1)
O(2)–In(1)–N(4)	80.5 (1)		
O(1)–Na(1)–O(3)	71.4 (1)	O(3)–Na(1)–O(8)	167.7 (3)
O(1)–Na(1)–O(4)	156.6 (3)	O(4)–Na(1)–O(5)	50.4 (3)
O(1)–Na(1)–O(5)	107.4 (2)	O(4)–Na(1)–O(7)	104.4 (3)
O(1)–Na(1)–O(7)	96.4 (2)	O(4)–Na(1)–O(8)	93.9 (4)
O(1)–Na(1)–O(8)	96.8 (3)	O(5)–Na(1)–O(7)	154.2 (3)
O(3)–Na(1)–O(4)	98.3 (3)	O(5)–Na(1)–O(8)	97.2 (3)
O(3)–Na(1)–O(5)	90.0 (2)	O(7)–Na(1)–O(8)	89.5 (3)
O(3)–Na(1)–O(7)	88.3 (2)		

three structures are included as supplementary material (see paragraph at the end of the paper).

Results

Ligand Synthesis. H_3L3 was readily prepared by a slight modification of the previously reported method.[21] The white trihydrochloride salt was isolated by adding a large excess of NH_4Cl to the reduction mixture. The analytical and spectral data are consistent with the proposed formulation. The presence of HCl was confirmed by the X-ray structure determination of the complex [Ga(HL3)]Cl·$CHCl_3$, which was obtained by the reaction of gallium(III) nitrate with H_3L3·3HCl·H_2O in the presence of excess sodium hydroxide.

Aluminum Complexes. All three ligands form easily isolable aluminum complexes [Al(HL)]ClO_4 (L = L1, L2, L3). Chelation of the metal ion proceeds in the presence of acetic acid, which is produced during the reaction of Al^{3+} with the ligand in the presence of sodium acetate trihydrate. As a result, one of the four nitrogen atoms of the amine phenol ligand is protonated and the complexes were isolated as perchlorate salts. All three complexes are soluble in DMSO and slightly soluble in methanol and acetone and are stable to air and moisture.

The FAB mass spectra of the aluminum complexes exhibit the expected peaks corresponding to $[Al(HL)]^+$ (L = L1, L2, L3). The compounds all show IR bands at 3270–3140 cm^{-1} from N–H stretches of the coordinated secondary amine groups and at 1600–1550 cm^{-1} from N–H bending vibrations. Upon coordination to the metal ion, the N–H bends undergo a general bathochromic shift (~20 cm^{-1}). Broad bands in the region 3650–3000 cm^{-1} due to O–H stretches suggest hydrogen bonding in the complexes. The splitting of the bands at about 1100 cm^{-1} is indicative of the hydrogen-bonded perchlorate anion in complexes [Al(HL)]ClO_4 (L = L1, L2, L3). New bands appear below 600 cm^{-1} in the spectrum of each coordinated ligand, and they are most likely ν_{M-O} or ν_{M-N}; however, exact assignments of these bands are difficult.

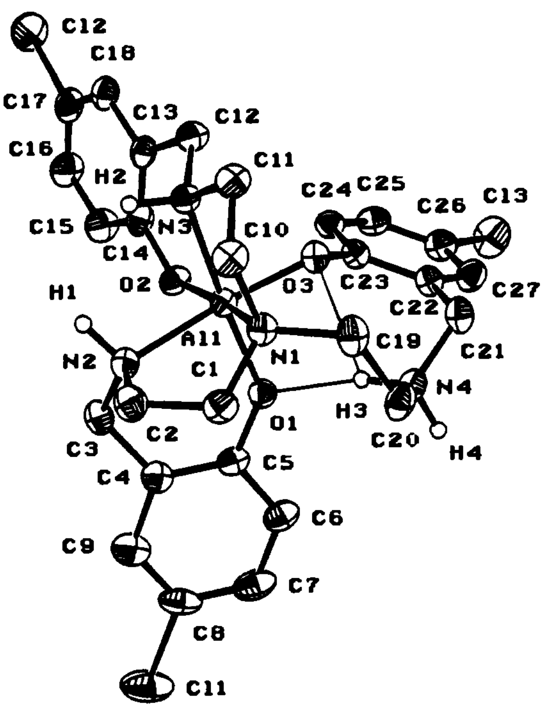

Figure 1. ORTEP drawing of $[Al(HL2)]^+$ in [Al(HL2)]ClO_4·2CH_3-OH.

An ORTEP drawing of $[Al(HL2)]^+$ is illustrated in Figure 1. The selected bond lengths and bond angles are listed in Table II. There is only one asymmetric complex cation $[Al(HL2)]^+$, a perchlorate anion, and two hydrogen-bonded methanols in each triclinic unit cell. The Al atom is coordinated by an N_3O_3 donor set from the N_4O_3 amine phenol ligand leaving N(4) uncoordinated. The coordination geometry is distorted octahedral with all three phenolate O atoms, and three (N(1), N(2), and N(3)) of the four N atoms, each trio facially coordinating to the Al atom. Each of the three chelating arms of the N_4O_3 amine phenol ligand binds to the metal center differently. The N(4)–O(3) arm is monodentate with N(4) protonated and O(3) coordinating to the Al^{3+} ion. The remaining two arms adopt different configurations with N(1), N(2), and O(1) facially coordinating, while the N(1), N(3), and O(2) arm binds meridionally, to the Al atom. The hydrogen atom at N(3) points toward the opposite side of the molecule to the O(3) atom. The Al–O distances in $[Al(HL2)]^+$ are 1.838, 1.824, and 1.819 Å for Al(1)–O(1), Al(1)–O(2), and Al(1)–O(3), respectively, with an average of 1.827 Å while the Al–N bond lengths are 2.207, 2.095, and 2.056 Å for Al(1)–N(1), Al(1)–N(2), and Al(1)–N(3), respectively. All three trans N–Al–O angles are approximately 170° due, in part, to the intrinsically small bite angles of the adjacent 5-membered chelate rings $AlNCH_2CH_2NH$ and, in part, to the constraints imparted by the protonated N(4) atom. This is consistent with the long Al(1)–N(1) distance (2.207 Å). Examples of structurally characterized Al complexes of hexadentate ligands are quite rare; to our knowledge, only three such examples have been re-

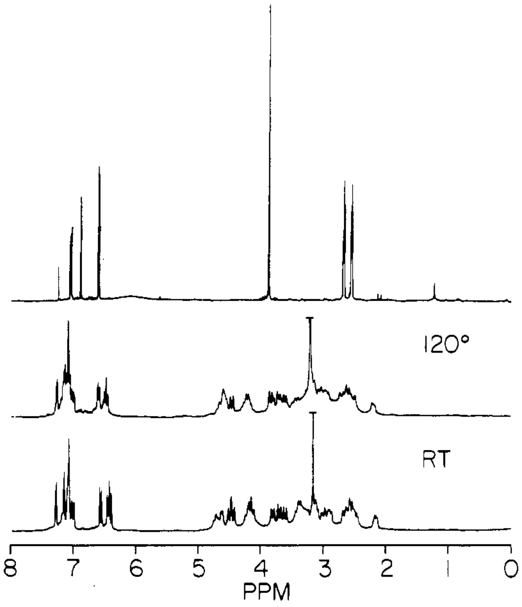

Figure 2. ^{1}H NMR spectra of H_3L2 (top) in $CDCl_3$ at room temperature (500 MHz) and of $[Al(HL2)ClO_4 \cdot 2CH_3OH$ in DMSO-d_6 at room temperature (bottom) and 120 °C (middle) (300 MHz).

ported.[24-26] One is $[Al(edta)]^-$,[24] another is alumichrome A[25] (Al substituting for Fe in ferrichrome A), and the third is (tren)-$Al[(CH_3)CN(CH_3)CN]_3$,[26] which is the reaction product of trimethylaluminum with tris(2-aminoethyl)amine and acetonitrile.

The ^{1}H NMR spectra of the three aluminum complexes in DMSO-d_6 were all very similar except in the aromatic region. One example ($[Al(HL2)]^+$) is shown in Figure 2. Due to the complexity of these spectra, detailed assignments were not made. In the uncomplexed amine phenol (Figure 2), all three chelating arms are equivalent; upon coordination to the metal center, however, these three arms become nonequivalent due to the asymmetric binding of the ligand to Al^{3+}. The amine phenol signals are split into three groups in the spectrum of the complex in DMSO-d_6. The signals (singlet at ~4.0 ppm) from hydrogens on C_c, and those from hydrogens on C_b and C_a (an A_2B_2 pattern at ~2.5 ppm) in the spectrum of the uncomplexed amine phenol ligand are split into several overlapped multiplets in the region of 2.0–5.6 ppm in the spectrum of the aluminum complex. These stay as multiplets to 120 °C (Figure 2). These observations clearly demonstrate that the rigid structure of this complex in DMSO is consistent with the structure of $[Al(HL2)]^+$ by X-ray diffraction methods. This conclusion is also supported by the ^{13}C spectra of the Al complex, which shows 27 distinct resonance signals from 27 different carbon atoms of the coordinated amine phenol ligand. If the complex were fluxional, only nine carbon resonance signals would be expected (as in the spectrum of the uncomplexed amine phenol[21]). Variable-temperature (21–120 °C) ^{1}H NMR spectra were obtained for all three aluminum complexes to examine fluxionality in DMSO solution. There is no significant change in each set of spectra except that there were some slight shifts of all the hydrogen signals; these shifts are probably caused by the thermal vibrations of the coordinated ligand framework.

Gallium Complexes. Reactions of H_3L1 with $Ga(NO_3)_3 \cdot 9H_2O$ in the presence of sodium acetate trihydrate or sodium hydroxide produces the identical product, $[Ga(HL1)]NO_3$, as shown by IR, NMR, FAB-MS, and elemental analysis. The complex $[Ga(HL3)]Cl \cdot CHCl_3$ was isolated as pale pink crystals from the reaction of $H_3L3 \cdot 3HCl \cdot H_2O$ with $Ga(NO_3)_3 \cdot 9H_2O$ in presence of 6 equiv of sodium hydroxide. Attempts to isolate an analytically pure gallium complex of L2 failed. The IR spectrum of $[Ga(HL1)]NO_3$ is similar to that of the aluminum complex except that the absorptions from hydrogen-bonded perchlorate anion are replaced by those of nitrate at 1380 and 1280 cm^{-1}. The FAB mass spectra of both gallium complexes exhibit the expected peaks corresponding to $[Ga(HL)]^+$ (L = L1 and L3). Like those of their aluminum analogs, the ^{1}H NMR spectra of $[Ga(HL1)]^+$ and $[Ga(HL3)]^+$ in DMSO-d_6 both show rigid structures in DMSO solution, and they remain rigid at temperatures higher than 120 °C as demonstrated by variable-temperature ^{1}H NMR experiments.

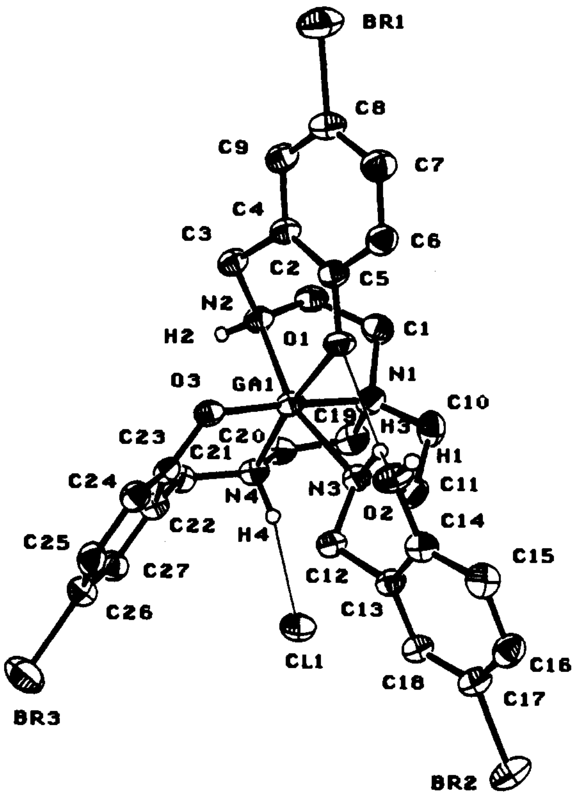

Figure 3. ORTEP drawing of $[Ga(HL3)]^+$ in $[Ga(HL3)]Cl \cdot CHCl_3$.

An ORTEP drawing of $[Ga(HL3)]Cl \cdot CHCl_3$ is illustrated in Figure 3; selected bond lengths and bond angles are listed in Table III. There are four chloroform-solvated $[Ga(HL3)]Cl$ molecules in the monoclinic unit cell, e.g. two pairs of enantiomers. The complex is cationic with Cl^- as the counterion; Cl^- bridges two nearest neighbor cations by forming hydrogen bonds with H(4) (Cl(1)- - -H(4) = 2.31 Å) of one $[Ga(HL3)]^+$ and H(2)-(Cl(1)- - -H(2) = 2.30 Å) of another. Hydrogen bonding is also observed between the Cl^- counterion and the chloroform hydrogen (Cl(1)- - -H(32) = 2.49 Å). Unlike the Al atom in $[Al(HL2)]^+$, the Ga atom is coordinated by an N_4O_2 donor set from the N_4O_3 amine phenol ligand, with one of three phenolate O atoms remaining uncoordinated and protonated (O(2)). The coordination geometry is distorted octahedral with N(1), N(2), and N(4) occupying one face of the octahedron and N(3), O(1), and O(2) occupying the other. The complex cation is chiral because of the ligand coordination to the metal center. One arm (N(1), N(2), and O(1)) facially coordinates to the Ga atom while another (N(1), N(4), and O(3)) meridionally binds to the Ga atom. N(3) and hydrogen H(4) on nitrogen N(4) are on the same side of the molecule. The Ga(1)–O(1) and Ga(1)–O(3) distances are 1.897 and 1.906 Å, respectively, close to the range 1.900–1.996 Å found in $[Ga(TX\text{-}TACN)H^+]$[14] and $Ga[(5\text{-}MeO\text{-}sal)_3tame]$.[27] The

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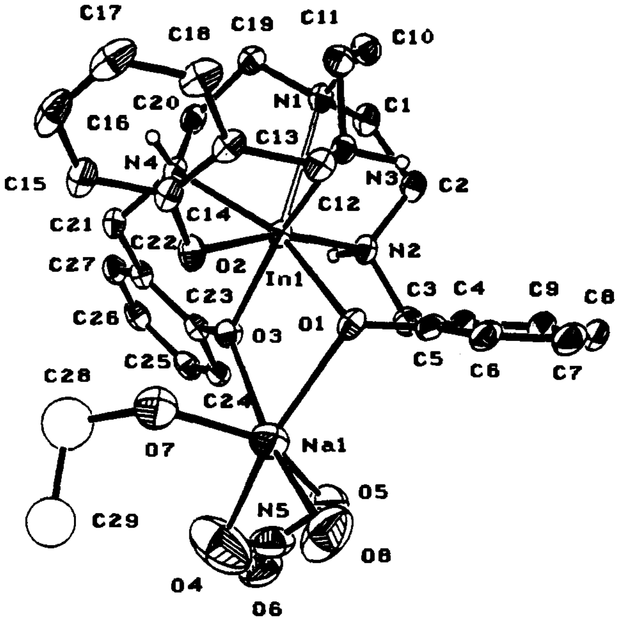

Figure 4. ORTEP drawing of $Na[In(L1)](NO_3)(H_2O)\cdot(C_2H_5OH)$.

Ga–N bond lengths range from 2.090 to 2.147 Å with an average of 2.113 Å, which compares well with those (2.097–2.221 Å) in Ga complexes of the N_3O_3[19,20] and N_3S_3[14] ligands.

The three trans angles, N(1)–Ga(1)–O(3), N(2)–Ga(1)–N(3), and N(4)–Ga(1)–O(1), are 172.7, 160.7, and 171.3°, respectively. The largest deviation from 180° (N(2)–Ga(1)–N(3)) is caused by the intrinsically small bite angle of two 5-membered $GaNCH_2CH_2NH$ chelate rings.[19] The N–Ga–N angles within the 5-membered chelate rings are approximately 81.5° while those between different chelate rings are larger (N(2)–Ga(1)–N(4) = 94.3°; N(3)–Ga(1)–N(4) = 94.4°). Most of the N–Ga–O angles are larger than 90° with the exception of N(3)–Ga(1)–O(1), which is probably lowered to 80.0° by the hydrogen bonding between H(3) and O(1)(O(1)- - -H(3) = 2.19 Å).

Indium Complexes. Unlike Al^{3+} and Ga^{3+}, In^{3+} forms neutral complexes, [In(L)] (L = L1, L2 and L3), with these N_4O_3 amine phenol ligands in the presence of a base (hydroxide or acetate). In $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$, sodium nitrate cocrystallizes with the complex. All the indium complexes are stable to air and moisture. They are all soluble in DMSO, slightly soluble in methanol and acetone, and insoluble in water. The analytical data of these complexes are consistent with the proposed formulations.

The FAB mass spectra of the three indium complexes show peaks corresponding to $[In(L)]^+$ and to $[In_2(L)]^+$ ($[M + In]^+$). In $Na[In(L1)](NO_3)$, a peak at m/z = 599 ($[M + Na]^+$) was also observed, indicating the presence of $NaNO_3$. This conclusion is supported by the IR spectra data, which show IR bands at 1380 and 1280 cm^{-1} due to the bidentate nitrate anion coordinating Na^+. The bidentate nature of nitrate anion was confirmed by the X-ray structure determination of $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$.

An ORTEP drawing of $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$ is illustrated in Figure 4. In each tetragonal unit cell there are 16 $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)$ molecules, e.g. eight pairs of enantiomers (Λ and Δ), and many partially occupied waters of the hydration. Every molecule in the unit cell is essentially independent. The complex is neutral with the In atom completely enclosed by the triply deprotonated N_4O_3 amine phenol ligand. Two phenolate O atoms (O(1) and O(3)) bridge the In and Na atoms (Na(1)–O(1) = 2.434 Å; Na(1)–O(3) = 2.449 Å); in addition, the Na atom is coordinated by two O atoms (Na(1)–O(4) = 2.43 Å; Na(1)–O(5) = 2.542 Å) of a bidentate nitrate anion, one water O atom (Na(1)–O(8) = 2.419 Å), and an ethanolic O atom (Na(1)–O(7) = 2.415 Å). Neglecting the phenolate-bridged Na atom and its donor atoms, the complex [In(L1)] has a 3-fold axis (the N1–In vector).

There are three geometries available to the coordinated heptadentate N_4O_3 amine phenol ligand: a trigonal prism capped on a triangular face, a trigonal prism capped on a square face, or a monocapped octahedron;[28] the coordination geometry around the In atom is a monocapped distorted octahedron. Trigonal prismatic coordination is obviated because the three chelating arms of the N_4O_3 amine phenol ligand would leave the apical N(1) atom far removed from the metal center. The apical nitrogen (In(1)–N(1) = 2.752 Å) caps the triangular face formed by the other three coordinating nitrogen atoms. This leads to a spreading of the N_3 face (N(2)–In(1)–N(3) = 105.3°; N(2)–In(1)–N(4) = 106.5°; N(3)–In(1)–N(4) = 107.9°) and a pinching of the O_3 face (O(1)–In(1)–O(2) = 85.3°; O(1)–In(1)–O(3) = 82.3°; O(2)–In(1)–O(3) = 85.4°) of the octahedron. The trans N–In–O angles and O–In–O angles average 162.9 and 84.3°, respectively, while the N–In–N angles (excluding N(1)) average 106.6°. The chelate N–In–O and N(1)–In–N angles average, respectively, 84.7 and 67.8°. These are very close to those in a related seven-coordinate complex [Yb(trac)][29] except that the apical nitrogen atom in [In(L1)] binds weakly to the metal center while in [Yb(trac)] it strongly binds to the Yb atom (Yb–N = 2.43 Å). This is probably due to the smaller size of In^{3+} relative to that of Yb^{3+}. The In–O distances are 2.177, 2.174, and 2.155 Å for In(1)–O(1), In(1)–O(2), and In(1)–O(3), respectively. The average In–secondary N bond lengths is 2.330 Å while the In–N(tertiary) distance is 2.752 Å. These values compare well to those found in two indium complexes of tricarboxylatotetraazamacrocycles (average In–N bond lengths: 2.36 and 2.42 Å),[30] with coordination geometries which are trigonal prisms capped on a square face. Unlike the aluminum and gallium complexes, the heptadenticity of the N_4O_3 amine phenol ligand in the indium complex [In(L1)] has been accomplished without imparting too much strain on the coordinated ligand framework. Furthermore, the indium complex in this study represents one of relatively few examples of a structurally characterized seven-coordinated metal complex containing only heptadentate ligands.[29-32]

The ^1H NMR spectra of the complexes [In(L)] (L = L1, L2, L3) in DMSO-d_6 are very similar (except for small differences in the aromatic hydrogen region 6.5–7.5 ppm), and only the spectrum (Figure 5) of [In(L1)] is discussed in detail. The spectra of all three [In(L)] complexes are much simpler than those of their aluminum and gallium analogues in the same solvent. Assignments (Table V) were carried out using ^1H–^1H COSY spectra and those of the uncomplexed amine phenol ligands.[21] The hydrogens H_e and H_f of the coordinated amine phenol ligand were distinguished by the fact that ring hydrogens in pseudoaxial environments are usually more shielded than those in pseudoequatorial environments.[33]

In the uncomplexed amine phenol, two hydrogen atoms H_e and H_f are equivalent and the same is true for the pairs H_a, H_b and H_c, H_d. There is only a singlet at 3.8 ppm from hydrogens H_e, H_f, and an A_2B_2 pattern at 2.5 ppm from hydrogens H_a, H_b, H_c, H_d in the ^1H spectrum ($CDCl_3$) of H_3L1.[21] Upon coordination to the metal center, the singlet at 3.8 ppm is split into two broad doublets at 5.1 and 3.4 ppm in the spectrum of [In(L1)] while the other part of the spectrum remains relatively unchanged (an A_2B_2 multiplet at ~2.5 ppm). The doublet at ~3.4 ppm is

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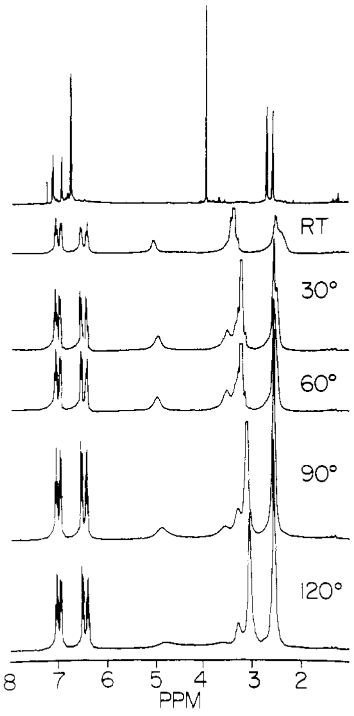
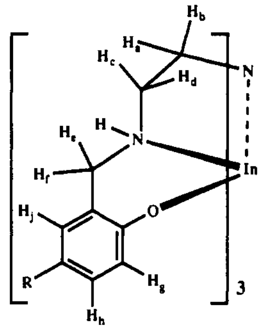


Figure 5. ^1H NMR spectra of H_3L1 (top) in $CDCl_3$ at room temperature (500 MHz) and of [In(L1)] in DMSO-d_6 at varying temperatures (300 MHz).

Table V. ^1H NMR Spectra Data for Indium Complexes with Amine Phenols (DMSO-d_6, δ in ppm from TMS)[a]



[In(L1)] (R = H_i)	[In(L2)] (R = Cl)	[In(L3)] (R = Br)	assignt
2.40 (m)	2.45 (m)	2.45 (m)	H_a, H_b, H_c, H_d
3.40 (bd)	3.45 (bd)	3.48 (bd)	H_e
5.10 (bd)	4.86 (bd)	4.86 (bd)	H_f
6.58 (d)	6.40 (d)	6.38 (d)	H_g
7.05 (t)	6.96 (d)	7.08 (d)	H_h
6.40 (t)			H_i
6.95 (d)	6.93 (s)	7.04 (s)	H_j

[a] Note: $^2J_{H-H} = 13.6$ Hz; $^3J_{H-H} = 6.8$–7.0 Hz.

overlapped with the signals of the H_2O and CH_3OH solvate molecules in DMSO-d_6. The Na^+ ion bridged by two phenolate O atoms in $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$ is dissociated in DMSO to give a symmetrical (C_3), presumably still seven-coordinated, species [In(L)]. The C_3 symmetry is also supported by ^{13}C NMR data of the complex, which, unlike its aluminum and gallium analogs, shows nine distinct resonance signals in its ^{13}C spectrum. The observation of two broad doublets for H_e and H_f is significant; this suggests that at room temperature all three chelating arms are equivalent even though they have been shown to be nonequivalent in the solid state (Figure 4). The complex in solution is relatively rigid and no inversion at the coordinated N atoms is taking place. If inversion at the coordinated N atoms took place, it would interchange the two hydrogens on each methylene carbon atom and a singlet from hydrogens H_e and H_f would be expected as found in the spectrum of H_3L1.[21] In addition, the small changes in the ethylene region (2.5–3.0 ppm) suggest that the interaction between the central nitrogen N(1) and the In atom is weak and that the three NCH_2CH_2N units remain relatively flexible. This is consistent with the solid-state structural findings in $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)\cdot 2.65H_2O$.

At elevated temperatures (>30 °C) the doublet at 5.1 ppm and the multiplet at ~2.5 ppm both become very broad singlets. At 120 °C (Figure 5), the broad singlet at 5.1 ppm starts to merge with the one at about 3.3 ppm. Higher temperature spectra of the complex were not obtained, but these two broad singlets are expected to become a singlet at temperatures above 120 °C. The collapse of the doublet at about 5.1 ppm is significant; it clearly shows that at high temperatures inversion at the coordinated N atoms occur. This contrasts with the high rigidity of the aluminum- and gallium-amine phenol complexes, which have distorted octahedral coordination geometries and strained ligands.

Discussion

Previously, these three potentially heptadentate (N_4O_3) tripodal amine phenols were found to form lanthanide complexes of two types $[Ln(H_3L)](NO_3)_3$ and $[Ln(L)]_2$, depending on the conditions of preparation.[21] For large lanthanide ions (ionic radii in six coordination: 1.03 Å for La^{3+} to 0.86 Å for Lu^{3+}),[34] the cavity of the N_4O_3 amine phenol ligand is too small to completely enclose the metal ion. This is, at least partially, responsible for the formation of dinuclear lanthanide complexes $[Ln(L)]_2$ (Ln = La, Nd, Pr, Gd, Dy; L = L1, L2, L3).[21] The structural data from the present study clearly show that the cavity of the N_4O_3 amine phenol ligand is too large for all seven donor atoms to coordinate to Al^{3+} (0.53 Å) or Ga^{3+} (0.62 Å); therefore, cationic aluminum and gallium complexes were isolated. In the crystal structure of $[Al(HL2)]ClO_4\cdot 2CH_3OH$, the Al atom is bonded to an N_3O_3 donor set with N(4) of the amine phenol ligand being protonated and uncoordinated, while the Ga atom in $[Ga(HL3)]Cl\cdot CHCl_3$ is coordinated by four amine N and two phenolate O donor atoms with the remaining phenolate O atom being protonated and uncoordinated. In both cases, the uncoordinated donor atoms impart certain steric constraints on the coordinated ligand framework, this, in turn, lowers the stability of the metal complexes. The cavity of the N_4O_3 amine phenol ligand seems to match In^{3+} (0.80 Å) best. Reaction of H_3L1 with In^{3+} in presence of a base such as sodium hydroxide produces a neutral indium complex $Na[In(L1)](NO_3)(H_2O)(C_2H_5OH)$, in which the In atom is coordinated by all seven (N_4O_3) donor atoms in a face-capped distorted octahedral coordination geometry without significant constraints on the coordinated framework.

It is notable that the Al atom in $[Al(HL2)]^+$ is coordinated by an N_3O_3 donor set, while the Ga atom in $[Ga(HL3)]^+$ is bonded to four amine N and two phenolate O atoms from the amine phenol ligand. This is related to the selectivity of Al^{3+} for negatively charged hard O donors over neutral N donors. Ga^{3+}, which also has a very strong affinity for phenolate O donors, also binds well with saturated amine N donors.[35] Thus, under the constraints imposed by the tripodal framework of the N_4O_3 amine phenol ligand, the Ga atom in $[Ga(HL3)]Cl\cdot CHCl_3$ is coordinated by an N_4O_2 donor set. Like Ga^{3+}, In^{3+} also has a strong affinity for both phenolate O donors and saturated amine N donors. Because of the larger size of In^{3+}, the coordination of all seven donor atoms is observed.

The octahedron is usually rather rigid, and fluxional rearrangements often occur in octahedral complexes with metal–ligand bond breaking. The aluminum and gallium complexes reported here have distorted octahedral coordination geometries.

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It is not surprising that these complexes remain very rigid in DMSO solution at temperatures higher than 120 °C. For the In complexes, however, the larger size makes it possible for all seven (N_4O_3) donor atoms to coordinate to the In atom to give a face-capped octahedral coordination geometry. The stereochemical nonrigidity is characteristic of seven-coordinate complexes, in which the energy difference between different stereochemistries (capped trigonal prism and monocapped octahedron) is very small.[36] Thus, all three chelating arms become equivalent in solution at room temperature although they have been shown to be nonequivalent in the solid state. This is presumably caused by interconversion of different stereochemistries. This conclusion is consistent with fact that the signals from the hydrogens of the three ethylene groups appear as an A_2B_2 pattern at 2.5 ppm instead of an ABCD spectrum as expected for a rigid five-membered chelate ring, $MNCH_2CH_2N$.[37] At higher temperatures, the two broad doublets collapse and are expected to give a singlet at the high-temperature limit. The only way for this to occur is through a dissociative inversion at the coordinated secondary amine N atoms because the interconversion of stereochemistries does not change the chirality of the coordinated pyramidal N atoms. For NH_3 and other simple noncyclic amines, the rate of inversion at N is extremely high (e.g., 2.4×10^{10} s^{-1} for NH_3).[38] When the polydentate ligand binds to the metal ion, inversion at a coordinated N atom becomes very difficult unless metal–ligand bond breaking is involved. In the aluminum and gallium complexes, the coordinated amine phenol ligands are so rigid that any movement of the framework has to overcome a very high energy barrier. In the indium complexes, the larger size of In^{3+} makes it possible for N1 to move around and take turns with the three secondary N atoms in bonding to the metal center to give a six-coordinate intermediate, $[In(N_3O_3)]$. Therefore, an intramolecular dissociative inversion at the coordinated N atoms in indium complexes occurs at temperatures higher than 120 °C, where the Al and Ga complexes remain rigid.

Conclusions

The coordination behavior of tripodal N_4O_3 amine phenols is largely dependent on the size of the coordinated metal ions. For large lanthanide ions, they form homodinuclear complexes, $[Ln(L)]_2$, under basic conditions. For the smaller group 13 metal ions (ionic radii 0.53 Å for Al^{3+} and 0.62 Å for Ga^{3+}), cationic complexes $[M(HL)]X$ (M = Al and Ga) were formed. The donor atoms in these complexes are dependent on the donor atom selectivity of the metal ion. Shortening of one of the three chelating arms or changing the tertiary N-bridged framework to a C-bridged framework (based on 1,1,1-tris(aminomethyl)ethane, 1,2,3-triaminopropane, or 1,2,3-triamino-2-methylpropane) will release the constraints imposed by the uncoordinated donor atoms and should produce potentially hexadentate N_3O_3 amine phenol ligands better tailored for six-coordinate neutral aluminum, gallium, and indium complexes. This prediction has been verified by initial structural studies of aluminum and gallium complexes with 1,1,1-tris(aminomethyl)ethane-based and 1,2,3-triaminopropane-based N_3O_3 amine phenol ligands.[39] The cavity of the N_4O_3 amine phenols seems to match best the size of In^{3+} (0.80 Å) and should form six- or seven-coordinate complexes of other trivalent metal ions, with ionic radii of about 0.80 Å.

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Supplementary Material Available: Complete tables of crystallographic data (Table SI), bond lengths (Tables SII–SIV), bond angles (Tables SV–SVII), hydrogen atom parameters (Tables SVIII–SX), anisotropic thermal parameters (Tables SXI–SXIII), torsion angles (Tables SIV–SXVI), intermolecular contacts (Tables SXVII–SXIX), least-squares planes (Tables SXX–SXXII), and final atomic coordinates and equivalent isotropic thermal parameters (Tables SXXVI–SXXVII) (70 pages). Ordering information is given on any current masthead page.

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