

# Highly Flexible Chelating Ligands for Group 13 Metals: Design and Synthesis of Hexadentate ( $N_3O_3$ ) Tripodal Amine Phenol Ligand Complexes of Aluminum, Gallium, and Indium

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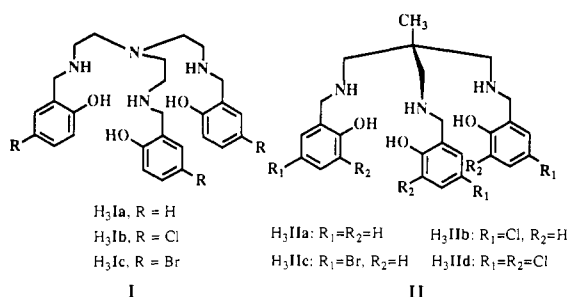
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New, potentially hexadentate ( $N_3O_3$ ) amine phenol ligands ( $H_3IIa = 1,1,1$ -tris(((2'-hydroxybenzyl)amino)methyl)ethane;  $H_3IIb = 1,1,1$ -tris(((5'-chloro-2'-hydroxybenzyl)amino)methyl)ethane;  $H_3IIc = 1,1,1$ -tris(((5'-bromo-2'-hydroxybenzyl)amino)methyl)ethane;  $H_3IIId = 1,1,1$ -tris(((3',5'-dichloro-2'-hydroxybenzyl)amino)methyl)ethane) have been prepared and characterized by various spectroscopic methods (IR, FAB-MS, NMR). The  $N_3O_3$  amine phenols are  $KBH_4$  reduction products of the corresponding Schiff bases derived from the condensation reactions of 1,1,1-tris(2-aminomethyl)ethane (tame) with 3 equiv of either salicylaldehyde or ring-substituted salicylaldehydes. Neutral binary metal complexes,  $[M(L)]$  ( $M = Al, Ga, In; L = IIa, IIb, IIc, IIId$ ) were obtained from the reactions of  $Al^{3+}$ ,  $Ga^{3+}$ , or  $In^{3+}$  with  $N_3O_3$  amine phenols in the presence of 3 equiv of a base (acetate or hydroxide). The molecular structures of  $\{[Al(IIc)]_4[Na(H_2O)]_2(ClO_4)_2\} \cdot 6.2H_2O$ ,  $[Ga(IIa)] \cdot 4.4H_2O$ , and  $[In(IIa)] \cdot 4.6H_2O$  were determined by X-ray methods. Crystals of  $\{[Al(IIc)]_4[Na(H_2O)]_2(ClO_4)_2\} \cdot 6.2H_2O$  are orthorhombic,  $Pbcn$ ,  $a = 27.226$  (2) Å,  $b = 15.687$  (4) Å,  $c = 30.013$  (3) Å, and  $Z = 4$ , and those of  $[Ga(IIa)] \cdot 4.4H_2O$  and  $[In(IIa)] \cdot 4.6H_2O$  are isomorphous, crystallizing in the monoclinic space group  $C2/c$ ,  $a = 32.105$  (9) Å [32.654 (2) Å],  $b = 10.559$  (2) Å [10.744 (2) Å],  $c = 19.626$  (5) Å [19.429 (2) Å],  $\beta = 118.43$  (1)° [117.842 (4)°], and  $Z = 8$  (bracketed values refer to the In complex). The structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to  $R = 0.049, 0.039$ , and  $0.038$  for 5668, 4028, and 4625 reflections with  $I \geq 3\sigma(I)$  for the Al, Ga, and In complexes, respectively. In these three complexes, the metal atoms (Al, Ga, and In) are all coordinated by six ( $N_3O_3$ ) donor atoms in distorted octahedral coordination geometries. As the metal ion becomes larger, the amine phenol ligand accommodates the coordinated metal ion in a subtle fashion, such that there are no significant identifiable bond angle increases, suggesting that the ligand backbone is extremely flexible. Variable-temperature  $^1H$  NMR spectral data revealed rigid solution structures for all aluminum, gallium, and indium complexes, with no evidence for fluxional behavior; the complexes remained very rigid at solution temperatures higher than 150 °C.

## Introduction

We are interested in the polydentate ligand 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. Recently we reported three  $N_4O_3$  tripodal amine phenols ( $H_3Ia, R = H; H_3Ib, R = Cl; H_3Ic, R = Br$ ; in which the chelating arms are bridged by a tertiary nitrogen atom) and their complexes of lanthanides and the group 13 metals (Al, Ga, In).<sup>2,3</sup> The



coordination behavior of the  $N_4O_3$  amine phenols is largely dependent on the size and properties of the bonded metal ions. For large lanthanide ions, the cavity is too small for an  $N_4O_3$

amine phenol ligand to enclose completely the metal center; homodinuclear complexes,  $[Ln(L)]_2$ , are formed under basic conditions.<sup>2</sup> For small group 13 metal ions ( $Al^{3+}$  and  $Ga^{3+}$ ), however, the cavity is too large for all seven donors to coordinate to the metal ion; therefore, six-coordinate cationic aluminum and gallium complexes were isolated.<sup>3</sup> The donor sets in these complexes depend on the affinity of the  $Al^{3+}$  or  $Ga^{3+}$  ions for neutral amine N and negatively charged phenolate O donors. The cavity of the  $N_4O_3$  amine phenol ligand seems to match  $In^{3+}$  best; seven-coordinated neutral indium complexes,  $[In(L)]$  ( $L = Ia, Ib$  and  $Ic$ ) were obtained. In the aluminum and gallium complexes, the uncoordinated donor atoms impart certain constraints on the coordinated ligand frameworks; this, in turn, would lower the stability of these metal complexes. In order to solve this problem, we decided to use tame (1,1,1-tris(aminomethyl)ethane) as the tripodal framework to produce a hexadentate ( $N_3O_3$ ) ligand system.

The gallium(III) complexes of the hexadentate ( $N_3O_3$ ) ligands 1,4,7-tris(3,5-dimethyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (TX-TACNH<sub>3</sub>) and 1,4,7-triazacyclononane-1,4,7-triacetic acid (NOTA) have been reported.<sup>5-7</sup> Both ligands, in which three chelating O-containing arms are attached to the nitrogen atoms of the macrocycle 9-aneN<sub>3</sub> to constitute an  $N_3O_3$  donor set, form very stable gallium and indium complexes.<sup>8,9</sup> Neutral lipophilic gallium complexes with hexadentate Schiff bases (e.g.

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1,1,1-tris((5-methoxysalicylaldimino)methyl)ethane) have also been reported.<sup>10-12</sup> Biodistribution experiments showed decomposition of the Schiff base complexes in vivo, suggesting the binding of the metal to liver macromolecules or its precipitation as gallium hydroxide.<sup>10</sup> The coordination chemistry of tame-based  $N_3O_3$  Schiff base ligands with transition metals<sup>12-17</sup> and group 13 metals<sup>18,19</sup> has also been investigated; however, the amine phenol ligands ( $H_3IIa-H_3IIId$ ), which we have prepared by the reduction of the Schiff bases, have not been previously reported.

Since the three chelating arms in  $N_3O_3$  amine phenols are bridged by a carbon atom, they cannot undergo a tertiary N atom "umbrella" type inversion as their  $N_4O_3$  analogs may. Therefore, the  $N_3O_3$  amine phenols can be considered to be more preorganized than their  $N_4O_3$  analogs. Because of the strong affinity of  $Al^{3+}$ ,  $Ga^{3+}$  and  $In^{3+}$  for amine N and phenolate O donors,<sup>20</sup> the  $N_3O_3$  amine phenol ligands are expected to form very stable neutral complexes with group 13 metal ions. Unlike imine  $CH=N$  linkages in Schiff bases, the  $CH_2-NH$  functionality in amine phenols is very stable with respect to hydrolytic decomposition. In addition, the substituents on the aromatic benzene rings can be varied in order to modify the lipophilicity of a metal complex while retaining the same coordination environment.

As a continuation of our investigation into the polydentate coordination chemistry of group 13 metals, we now present the synthesis, structures and characterization of a new series of potentially hexadentate tripodal amine phenols ( $H_3IIa-H_3IIId$ ) and of their aluminum, gallium and indium complexes. We were determined to retain the tribasic character in the ligand in order to conserve the overall neutral complex charge, an important factor for the in vivo mobility of metal complex imaging agents.<sup>4</sup>

## Experimental Section

**Materials.** Potassium borohydride, lithium aluminum hydride, sodium azide, hydrated metal salts, 2-(hydroxymethyl)-2-methyl-1,3-propanediol, salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, and 3,5-dichlorosalicylaldehyde were obtained from Aldrich or Alfa and were used without further purification. 1,1,1-Tris((benzenesulfonyloxy)methyl)ethane and 1,1,1-tris(azidomethyl)ethane were prepared according to literature methods.<sup>21</sup>

**Instrumentation.** NMR spectra were recorded on Bruker AC-200E ( $^1H$ - $^1H$  COSY and APT  $^{13}C$  NMR), Varian XL 300 (VT NMR) and Varian XL 500 ( $^1H$ ,  $^{13}C$ ,  $^1H$ - $^{13}C$  heteronuclear correlation) spectrometers. Mass spectra were obtained with either a Kratos MS 50 (electron-impact ionization, EI) or an AEI MS-9 (fast-atom-bombardment ionization, FAB) instrument; only the most intense peaks are shown where envelopes from different isotopes were observed. Infrared spectra were recorded as KBr disks in the range of 4000-400  $cm^{-1}$  on a Perkin-Elmer PE 783 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 on a Carlo Erba instrument in this department.

**Ligand Synthesis.** *Caution! The handling of polyazides in large quantities may be hazardous. Perchlorate salts of metal complexes are potentially explosive and should be handled with care and only in small amounts.*

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**Table I.** Analytical Data (Calcd (Found)) for Al, Ga, and In Complexes of  $N_3O_3$  Amine Phenols

compound	C	H	N
[Al(IIa)]·6H <sub>2</sub> O	55.02 (54.51)	7.46 (7.04)	7.40 (7.34)
[Al(IIb)]	55.48 (55.11)	4.84 (4.97)	7.47 (7.17)
[Al(IIc)]·CH <sub>3</sub> OH	44.53 (44.29)	4.29 (4.22)	5.77 (5.81)
{[Al(IIc)] <sub>4</sub> [Na(H <sub>2</sub> O)] <sub>2</sub> ·(ClO <sub>4</sub> ) <sub>2</sub> ·6CH <sub>3</sub> OH·2H <sub>2</sub> O}	40.26 (40.05)	3.93 (4.07)	5.12 (5.23)
[Al(IIId)]	46.88 (46.62)	3.63 (3.57)	6.31 (6.17)
[Ga(IIa)]·3.5H <sub>2</sub> O	55.24 (55.22)	6.60 (6.35)	7.43 (7.06)
[Ga(IIb)]	51.57 (52.00)	4.49 (4.63)	6.94 (6.73)
[Ga(IIc)]	42.26 (42.20)	3.68 (3.15)	5.69 (5.60)
[Ga(IIId)]·1.5H <sub>2</sub> O	42.43 (42.41)	3.70 (3.89)	5.71 (5.43)
[In(IIa)]·6H <sub>2</sub> O	47.64 (47.92)	6.46 (6.40)	6.41 (6.45)
[In(IIb)]·3H <sub>2</sub> O	44.31 (44.64)	4.72 (4.53)	5.96 (5.81)
[In(IIc)]·2H <sub>2</sub> O	38.08 (38.00)	3.81 (3.94)	5.12 (5.03)
[In(IIId)]·H <sub>2</sub> O	40.45 (40.25)	3.39 (3.52)	5.44 (5.39)

**1,1,1-Tris(aminomethyl)ethane (tame).** Tame was prepared with some modifications to the reported method.<sup>21</sup> To a cold solution (on an ice-bath) of 1,1,1-tris(azidomethyl)ethane (16.8 g, 0.086 mol) in 200 mL of dry THF was added slowly LiAlH<sub>4</sub> (14 g) over a period of 30 min. After the addition was complete, the mixture was refluxed for 24 h. The mixture was cooled to 0 °C and then 8 M NaOH (20 mL) was added slowly to quench excess LiAlH<sub>4</sub>. To the resulting white slurry was added diethyl ether (500 mL) and the reaction mixture was stirred for 30 min. The white precipitate was removed and washed with diethyl ether (2 × 200 mL). The combined filtrate and washings were dried over anhydrous MgSO<sub>4</sub>. Removal of solvent on a rotary evaporator afforded a pale-yellow oil, 8.6 g (86%). IR and <sup>1</sup>H NMR spectra of the crude product were identical with those previously reported.<sup>21</sup> This crude product was used without further purification.

**1,1,1-Tris((salicylidene)imino)methyl)ethane (H<sub>3</sub>saltame).** To a solution of salicylaldehyde (3.6 g, 30 mmol) in absolute ethanol (5 mL) was added tame (1.17 g, 10 mmol) in the same solvent (5 mL). In 5 min, a yellow precipitate formed. The mixture was left standing at room temperature for 2-3 h and the solid was then filtered out, washed with diethyl ether and dried in air; the yield was 3.3 g (77%), mp 134.5-135 °C (lit.,<sup>13</sup> 134.8-135.5 °C). Anal. Calcd (found) for C<sub>26</sub>H<sub>27</sub>N<sub>3</sub>O<sub>3</sub>: C, 72.71 (72.61); H, 6.34 (6.49); N, 9.78 (9.84). Mass spectrum (EI): *m/z* = 429 ([C<sub>26</sub>H<sub>27</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>). IR (cm<sup>-1</sup>, KBr disk): 3200-2000 (br,  $\nu_{O-H}$ ), 3000-2800 (m or w,  $\nu_{C-H}$ ), 1630, 1580 and 1495 (vs,  $\nu_{C=N}$  and  $\nu_{C=C}$ ).

**1,1,1-Tris((5'-chlorosalicylidene)imino)methyl)ethane (H<sub>3</sub>-5-Cl(saltame)).** To a hot solution of 5-chlorosalicylaldehyde (4.7 g, 30 mmol) in absolute ethanol (150 mL) was added tame (1.17 g, 10 mmol) in 5 mL of the same solvent. The resulting yellow solution was refluxed for 30 min and then cooled to room temperature. Slow evaporation of the solvent afforded an orange-yellow solid, which was collected by filtration, washed with absolute ethanol followed by diethyl ether, and dried in air; the yield was 4.5 g (80%), mp 122-124 °C. Anal. Calcd (found) for C<sub>26</sub>H<sub>24</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>3</sub>: C, 58.61 (58.28); H, 4.54 (4.66); N, 7.89 (7.88). Mass spectrum (EI): *m/z* = 531 ([C<sub>26</sub>H<sub>24</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>). IR (cm<sup>-1</sup>, KBr disk): 3200-2000 (br,  $\nu_{O-H}$ ); 1635, 1577 and 1480 (vs,  $\nu_{C=N}$  and  $\nu_{C=C}$ ).

**1,1,1-Tris((5'-bromosalicylidene)imino)methyl)ethane (H<sub>3</sub>-5-Br(saltame)).** Using the same procedure as that for H<sub>3</sub>-5-Cl(saltame), 5-bromosalicylaldehyde (6.03 g, 30 mmol), was converted to its corresponding Schiff base; the yield was 4.5 g (80%), mp 135-137 °C. Anal. Calcd (found) for C<sub>26</sub>H<sub>24</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>3</sub>: C, 46.88 (47.38); H, 3.63 (3.89); N, 6.31 (6.15). Mass spectrum (EI): *m/z* = 665 ([C<sub>26</sub>H<sub>24</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>). IR (cm<sup>-1</sup>, KBr disk): 3600-2000 (w,  $\nu_{O-H}$ ); 3000-2800 (w or m,  $\nu_{C-H}$ ); 1640, 1575 and 1480 (vs,  $\nu_{C=N}$  and  $\nu_{C=C}$ ).

**1,1,1-Tris(((3',5'-dichlorosalicylidene)imino)methyl)ethane (H<sub>3</sub>-3,5-Cl<sub>2</sub>saltame).** It was prepared similarly to H<sub>3</sub>-5-Cl(saltame) from 3,5-dichlorosalicylaldehyde (5.73 g, 30 mmol) and tame (1.17 g, 10 mmol); the yield of yellow solid was 5.1 g (80%), mp 127-129 °C. Anal. Calcd (found) for C<sub>26</sub>H<sub>21</sub>Cl<sub>6</sub>N<sub>3</sub>O<sub>3</sub>·1.5H<sub>2</sub>O: C, 47.09 (47.00); H, 3.65 (3.29); N, 6.34 (6.45). Mass spectrum (EI): *m/z* = 635 ([C<sub>26</sub>H<sub>21</sub>Cl<sub>6</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>). IR (cm<sup>-1</sup>, KBr disk): 3600-2000 (w,  $\nu_{O-H}$ ); 3000-2800 (w or m,  $\nu_{C-H}$ ); 1640, 1590 and 1450 (vs,  $\nu_{C=N}$  and  $\nu_{C=C}$ ).

**1,1,1-Tris(((2'-hydroxybenzyl)amino)methyl)ethane (H<sub>3</sub>IIa).** To a solution of H<sub>3</sub>saltame (2.15 g, 5 mmol) in methanol (100 mL) was added KBH<sub>4</sub> (1.08 g, 20 mmol) in small portions at room temperature over 30 min. After the addition was complete, the reaction mixture was stirred at room temperature for an additional 2 h. The solvent was removed under reduced pressure. To the residue was added NH<sub>4</sub>OAc (3 g) in water (50 mL), and the mixture was extracted with chloroform (3 × 100

**Table II.** Infrared ( $\text{cm}^{-1}$ , KBr disk) and FAB Mass Spectral Data for Al, Ga, and In Complexes of  $\text{N}_3\text{O}_3$  Amine Phenols

compound	$\nu_{\text{O-H}}$ and $\nu_{\text{N-H}}$	$\delta_{\text{N-H}}$	[ML + 1] ( $m/z$ )	[2ML + 1] ( $m/z$ )
[Al(IIa)]·6H <sub>2</sub> O	3700–2700 bs; 3260 m	1600 s; 1572 w	460	919
[Al(IIb)]	3700–2800 bs; 3265 m	1600 s; 1570 w	562	
{[Al(IIc)] <sub>4</sub> [Na(H <sub>2</sub> O)] <sub>2</sub> · (ClO <sub>4</sub> ) <sub>2</sub> ·6CH <sub>3</sub> OH·2H <sub>2</sub> O}	3700–2800 bs; 3270 m	1595 s; 1560 w	698	
[Al(IIId)]	3700–3600 bs; 3265 m	1587 m; 1550 w	667	
[Ga(IIa)]·3.5H <sub>2</sub> O	3000–3650 bs; 3260 s	1598 s; 1570 m	502	1005
[Ga(IIb)]	3700–3000 bm; 3265 s	1590 s; 1560 w	605	
[Ga(IIc)]	3700–3000 bm; 3265 s	1594 s; 1560 w	740	
[Ga(IIId)]·1.5H <sub>2</sub> O	3700–2800 bs; 3275 s	1590 m; 1553 w	708	
[In(IIa)]·6H <sub>2</sub> O	3700–2800 bs; 3265 s	1598 s; 1565 m	548	1094
[In(IIb)]·3H <sub>2</sub> O	3700–2200 bs; 3260 s	1595 s; 1560 s	650	
[In(IIc)]·2H <sub>2</sub> O	3700–2500 bs; 3260 s	1585 s; 1565 s	784	
[In(IIId)]·H <sub>2</sub> O	3700–3000 bm; 3275 m	1585 m	753	

mL). The organic phases were combined, washed with water, and dried over anhydrous MgSO<sub>4</sub>. The solution was filtered and chloroform was removed on a rotary evaporator to afford a pale-yellow solid. The solid was dried under vacuum overnight; the yield was 1.9 g (87%), mp 65–68 °C. Anal. Calcd (found) for C<sub>26</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>·1.5H<sub>2</sub>O: C, 67.51 (67.70); H, 7.84 (7.74); N, 9.08 (9.07). Mass spectrum (FAB):  $m/z$  = 436 ([C<sub>26</sub>H<sub>34</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>, [M + 1]<sup>+</sup>). IR ( $\text{cm}^{-1}$ , KBr disk): 3300 (m,  $\nu_{\text{N-H}}$ ); 3600–2000 (m,  $\nu_{\text{O-H}}$ ); 3100–2800 (m or s,  $\nu_{\text{C-H}}$ ); 1615 and 1592 (s,  $\delta_{\text{N-H}}$ ); 1490–1420 (vs,  $\nu_{\text{C=C}}$ ).

**1,1,1-Tris((5'-chloro-2'-hydroxybenzyl)amino)methyl)ethane (H<sub>3</sub>IIb).** A procedure similar to that for H<sub>3</sub>IIa was followed using H<sub>3</sub>-5-Cl(saltame) (2.66 g, 5.0 mmol) in hot methanol (150 mL) and KBH<sub>4</sub> (1.08 g, 20 mmol); the yield was 2.50 g (73%) mp 61–63 °C. Anal. Calcd (found) for C<sub>26</sub>H<sub>30</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>3</sub>: C, 57.95 (57.60); H, 5.61 (5.74); N, 7.80 (7.28). Mass spectrum (FAB):  $m/z$  = 539 ([C<sub>26</sub>H<sub>31</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>, [M + 1]<sup>+</sup>). IR ( $\text{cm}^{-1}$ , KBr disk): 3320 (m,  $\nu_{\text{N-H}}$ ); 3600–2000 (m,  $\nu_{\text{O-H}}$ ); 3100–2800 (m or s,  $\nu_{\text{C-H}}$ ); 1615 and 1590 (s,  $\delta_{\text{N-H}}$ ); 1490–1420 (vs,  $\nu_{\text{C=C}}$ ).

**1,1,1-Tris((5'-bromo-2'-hydroxybenzyl)amino)methyl)ethane (H<sub>3</sub>IIc).** A procedure similar to that for H<sub>3</sub>IIa was followed using H<sub>3</sub>-5-Br(saltame) (2.66 g, 5.0 mmol) in hot methanol (150 mL) and KBH<sub>4</sub> (1.08 g, 20 mmol); the yield was 2.50 g (73%), mp 65–67 °C. Anal. Calcd (found) for C<sub>26</sub>H<sub>30</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>3</sub>·2H<sub>2</sub>O: C, 44.09 (44.29); H, 4.84 (4.60); N, 5.93 (5.73). Mass spectrum (FAB):  $m/z$  = 674 ([C<sub>26</sub>H<sub>31</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>, [M + 1]<sup>+</sup>). IR ( $\text{cm}^{-1}$ , KBr disk): 3320 (m,  $\nu_{\text{N-H}}$ ); 3500–2000 (m,  $\nu_{\text{O-H}}$ ); 1612 and 1582 (s,  $\delta_{\text{N-H}}$ ); 1490–1420 (vs,  $\nu_{\text{C=C}}$ ).

**1,1,1-Tris((3',5'-dichloro-2'-hydroxybenzyl)amino)methyl)ethane (H<sub>3</sub>IIId).** It was prepared similarly to H<sub>3</sub>IIa using H<sub>3</sub>-3,5-Cl<sub>2</sub>saltame (3.17 g, 5.0 mmol) in hot methanol (150 mL) and KBH<sub>4</sub> (1.08 g, 20 mmol); the yield was 2.4 g (73%), mp 92–95 °C. Anal. Calcd (found) for C<sub>26</sub>H<sub>27</sub>Cl<sub>6</sub>N<sub>3</sub>O<sub>3</sub>: C, 47.30 (47.10); H, 4.43 (4.15); N, 6.36 (6.45). Mass spectrum (FAB):  $m/z$  = 642 ([C<sub>26</sub>H<sub>28</sub>Cl<sub>6</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup>, [M + 1]<sup>+</sup>). IR ( $\text{cm}^{-1}$ , KBr disk): 3320 (m,  $\nu_{\text{N-H}}$ ); 3500–2000 (m,  $\nu_{\text{O-H}}$ ); 3100–2800 (m,  $\nu_{\text{C-H}}$ ); 1615 and 1590 (s,  $\delta_{\text{N-H}}$ ); 1490–1420 (vs,  $\nu_{\text{C=C}}$ ).

**Synthesis of Metal Complexes.** Since many of the syntheses were similar to each other, detailed procedures are only given for representative examples. All the complexes which were prepared, along with their analytical data are listed in Table I; infrared and FAB mass spectral data are in Table II.

**[Al(IIa)]·6H<sub>2</sub>O.** To a solution of Al(ClO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O (245 mg, 0.50 mmol) in methanol (25 mL) was added H<sub>3</sub>IIa·H<sub>2</sub>O (240 mg, 0.53 mmol) in the same solvent (10 mL). After the addition of NaOAc·3H<sub>2</sub>O (280 mg, 2.0 mmol) in methanol (10 mL), the resulting mixture was filtered immediately; slow evaporation yielded pink microcrystals, which were collected by filtration, washed successively with water, cold ethanol and diethyl ether. The yield was 200 mg (71%).

**[Al(IIc)]·CH<sub>3</sub>OH.** Solutions of Al(ClO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O (245 mg, 0.50 mmol) in methanol (25 mL) and of H<sub>3</sub>IIc (350 mg, 0.52 mmol) in chloroform (5 mL) were mixed. After the addition of LiOH·H<sub>2</sub>O (84 mg, 2.0 mmol) in water (10 mL), the solution was filtered immediately. Slow evaporation of solvents produced pink crystals. These were separated and washed successively with water, ethanol and diethyl ether. The yield was 450 mg (56%).

**{[Al(IIc)]<sub>4</sub>[Na(H<sub>2</sub>O)]<sub>2</sub>·(ClO<sub>4</sub>)<sub>2</sub>·6CH<sub>3</sub>OH·2H<sub>2</sub>O}.** Solutions of Al(ClO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O (245 mg, 0.50 mmol) in methanol (25 mL) and of H<sub>3</sub>IIc (350 mg, 0.52 mmol) in chloroform (5 mL) were mixed. After addition of 2 M NaOH solution (1 mL) dropwise, the solution was filtered immediately; evaporation of solvents afforded pink crystals. These were separated and washed successively with water, ethanol and diethyl ether.

**Table III.** Selected Crystallographic Data for {[Al(IIc)]<sub>4</sub>[Na(H<sub>2</sub>O)]<sub>2</sub>·(ClO<sub>4</sub>)<sub>2</sub>·6.22H<sub>2</sub>O}, [Ga(IIa)]·4.35H<sub>2</sub>O, and [In(IIa)]·4.57H<sub>2</sub>O

complex	{[Al(IIc)] <sub>4</sub> [Na(H <sub>2</sub> O)] <sub>2</sub> · (ClO <sub>4</sub> ) <sub>2</sub> ·6.22H <sub>2</sub> O}	[Ga(IIa)]· 4.35H <sub>2</sub> O	[In(IIa)]· 4.57H <sub>2</sub> O
formula	C <sub>104</sub> H <sub>120.44</sub> AlBr <sub>12</sub> · Cl <sub>2</sub> N <sub>12</sub> O <sub>9</sub> Na <sub>2</sub> O <sub>28.22</sub>	C <sub>26</sub> H <sub>38.7</sub> · GaN <sub>3</sub> O <sub>7.35</sub>	C <sub>26</sub> H <sub>39.14</sub> · InN <sub>3</sub> O <sub>7.57</sub>
fw	3173.78	580.63	629.69
cryst syst	orthorhombic	monoclinic	monoclinic
space group	<i>Pbcn</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> , Å	27.226(2)	32.105(9)	32.654(2)
<i>b</i> , Å	15.687(4)	10.559(2)	10.744(2)
<i>c</i> , Å	30.013(3)	19.626(5)	19.429(2)
$\beta$ , deg	90	118.43(1)	117.842(4)
<i>V</i> , Å <sup>3</sup>	12818(3)	5851(2)	6027(1)
<i>Z</i>	4	8	8
$\rho_c$ , g/cm <sup>3</sup>	1.644	1.318	1.388
<i>T</i> , °C	21	21	21
radiation ( $\lambda$ , Å)	Cu (1.541 78)	Cu (1.541 78)	Cu (1.541 78)
$\mu$ (Cu K $\alpha$ ), cm <sup>-1</sup>	58.36	16.49	67.81
transm factors	0.87–1.00	0.78–1.00	0.83–1.00
<i>R</i>	0.049	0.039	0.038
<i>R<sub>w</sub></i>	0.048	0.046	0.043

The yield was 450 mg (56%). Suitable crystals were selected for X-ray diffraction studies.

**[Ga(IIa)]·3.5H<sub>2</sub>O. Method 1.** To a solution of Ga(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (209 mg, 0.5 mmol) in methanol (20 mL) was added H<sub>3</sub>IIa·H<sub>2</sub>O (240 mg, 0.53 mmol) in the same solvent (10 mL). After dropwise addition of a 2 M NaOH solution (1 mL), the resulting mixture was filtered immediately. Slow evaporation of the solvents afforded pink crystals, which were collected by filtration, washed with cold ethanol followed by diethyl ether, and dried in air. The yield was 200 mg (71%).

**Method 2.** Solutions of Ga(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (209 mg, 0.50 mmol) in methanol (25 mL) and of H<sub>3</sub>IIa·H<sub>2</sub>O (240 mg, 0.53 mmol) in the same solvent (10 mL) were mixed. After addition of NaOAc·3H<sub>2</sub>O (280 mg, 2.0 mmol) in methanol (5 mL), the mixture was filtered immediately. The filtrate was left standing at the room temperature to evaporate solvents slowly until pink microcrystals formed. These were separated, washed with ethanol and diethyl ether, and dried in air. The yield was 205 mg (72%). The product was shown by IR and elemental analysis to be identical to that obtained by method 1.

**X-ray Crystallographic Analyses.** Selected crystallographic data for the three compounds appear in Table III. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with  $2\theta = 47.4$ – $55.6^\circ$  for {[Al(IIc)]<sub>4</sub>[Na(H<sub>2</sub>O)]<sub>2</sub>·(ClO<sub>4</sub>)<sub>2</sub>·6.22H<sub>2</sub>O},  $50.0$ – $70.6^\circ$  for [Ga(IIa)]·4.35 H<sub>2</sub>O, and  $55.0$ – $66.7^\circ$  for [In(IIa)]·4.6H<sub>2</sub>O. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed uniformly by 5.6% for {[Al(IIc)]<sub>4</sub>[Na(H<sub>2</sub>O)]<sub>2</sub>·(ClO<sub>4</sub>)<sub>2</sub>·6.22H<sub>2</sub>O} and by 5.0% for [In(IIa)]·4.6H<sub>2</sub>O and were essentially constant for [Ga(IIa)]·4.35 H<sub>2</sub>O. The data were processed and corrected for Lorentz and polarization effects, decay (for {[Al(IIc)]<sub>4</sub>[Na(H<sub>2</sub>O)]<sub>2</sub>·(ClO<sub>4</sub>)<sub>2</sub>·6.22H<sub>2</sub>O} and [In(IIa)]·4.6H<sub>2</sub>O), and absorption (empirical, based on azimuthal scans for three reflections).<sup>22</sup>

(22) TEXSAN/TEXRAY structure analysis package (Molecular Structure Corp., 1985) that 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.

The crystal structures of all three 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 analyses of  $[\text{Ga}(\text{IIa})]\cdot 4.35 \text{ H}_2\text{O}$  and the isomorphous complex  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$  were initiated in the centrosymmetric space group  $C2/c$ , based on the  $E$ -statistics and the Patterson functions, these choices being confirmed by the subsequent successful solutions and refinements of the structures.

The polynuclear  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2\}^{2+}$  cation in  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2\cdot 6.2 \text{ H}_2\text{O}$  has exact (crystallographic)  $C_2$  symmetry. The asymmetric unit of  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2\cdot 6.2 \text{ H}_2\text{O}$  contains two  $[\text{Al}(\text{IIc})]$  units, a sodium ion, the central water molecule of the cation, one perchlorate anion, and 3.11 water solvate molecules disordered over five sites (one of which, O(12), is fully occupied). The perchlorate anion displays a high degree of thermal motion and may be disordered, but no attempt to refine a disordered model was made. The site occupancy factor for O(13) was refined initially and kept fixed in the final stages of refinement. The occupancy factors for the remaining disordered water molecules were adjusted to give approximately equal thermal parameters. All non-hydrogen atoms except for the partially occupied water sites O(14), O(14A) and O(15) were refined with anisotropic thermal parameters. The only possible location for a methanol molecule in the solvent region is at the partially occupied positions O(14) and O(15) that are 1.24 (4) Å apart. The X-ray analysis is thus consistent with the presence of not more than one methanol molecule per tetranuclear complex.

The asymmetric units of  $[\text{Ga}(\text{IIa})]\cdot 4.4 \text{ H}_2\text{O}$  and  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$  contain the  $[\text{M}(\text{IIa})]$  ( $M = \text{Ga}$  and  $\text{In}$ ) complexes, one water molecule hydrogen-bonded to the complex O(4), a fully occupied site, and an additional 3.35 ( $M = \text{Ga}$ ) or 3.57 ( $M = \text{In}$ ) water molecules. For the Ga complex  $[\text{Ga}(\text{IIa})]\cdot 4.4 \text{ H}_2\text{O}$ , these additional water molecules were disordered over eight sites. Occupancy factors were refined for all eight partially occupied water sites and all of these partial oxygen atoms except O(6) were refined with anisotropic thermal parameters. In the indium structure  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$ , there are two additional fully occupied water sites (O(6) and O(7)) and four partially occupied sites. The occupancy factors for the partially occupied water sites were also refined for  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$ . All non-hydrogen atoms of  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$  except for the four partly occupied oxygen sites were refined with anisotropic thermal parameters.

The hydrogen atoms associated with the IIc ligands in  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2\cdot 6.2 \text{ H}_2\text{O}$  and the IIa ligands in  $[\text{Ga}(\text{IIa})]\cdot 4.4 \text{ H}_2\text{O}$  and  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$  were fixed in calculated positions ( $N\text{-H}/C\text{-H} = 0.98 \text{ \AA}$ ,  $B_{\text{H}} = 1.2 B_{\text{bonded atom}}$ ). The hydrogen atoms associated with O(4) in  $[\text{Ga}(\text{IIa})]\cdot 4.4 \text{ H}_2\text{O}$  and  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$ , were placed in difference map positions but were not refined. Hydrogen atoms associated with the disordered water molecules were not included in the model. Secondary extinction corrections were applied in all three cases, the final values of the extinction coefficient being  $2.09 \times 10^{-6}$ ,  $9.85 \times 10^{-6}$ , and  $1.45 \times 10^{-5}$ , respectively for  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2\cdot 6.2 \text{ H}_2\text{O}$ ,  $[\text{Ga}(\text{IIa})]\cdot 4.4 \text{ H}_2\text{O}$  and  $[\text{In}(\text{IIa})]\cdot 4.6 \text{ H}_2\text{O}$ . Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 23.

Final atomic coordinates and equivalent isotropic thermal parameters appear in Table IV, while selected bond lengths and bond angles for the three structures appear in Tables V–VII. Complete tables of crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond distances and angles, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.

## Results and Discussion

**Ligand Synthesis.** Tame (1,1,1-tris(aminomethyl)ethane) was prepared according to the previously reported method<sup>21</sup> with some modifications.  $\text{N}_3\text{O}_3$  Schiff bases were obtained from the condensation reaction of tame with 3 equiv of salicylaldehyde or its ring-substituted derivatives (Scheme I). Subsequent reduction of these Schiff bases by  $\text{KBH}_4$  afforded the  $\text{N}_3\text{O}_3$  amine phenols. All four amine phenols are soluble in polar solvents such as chloroform, acetone and methanol. Unlike the analogous Schiff bases,<sup>10,11</sup> the  $\text{N}_3\text{O}_3$  amine phenols are hydrolytically stable in solution under either basic or acidic conditions.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for the Schiff bases and the amine phenols are summarized in Tables VIII–XI. The NMR spectral assignments were based on  $^1\text{H}$ – $^1\text{H}$  COSY and  $^1\text{H}$ – $^{13}\text{C}$  heteronuclear correlation with the attached proton test (APT) and on those previously reported for the  $\text{N}_4\text{O}_3$  analogs.<sup>2,3</sup> The analytical and spectral data are completely consistent with the proposed formulations. Infrared spectra of the amine phenols show the disappearance of some bands in the region 1630–1500  $\text{cm}^{-1}$  characteristic of the imine  $\text{C}=\text{N}$  bonds in the Schiff bases, and the appearance of two new bands at 1610–1580  $\text{cm}^{-1}$  from  $\text{N}-\text{H}$  bending vibrations. The  $^1\text{H}$  NMR data show the disappearance of  $\text{CH}=\text{N}$  hydrogen resonances at  $\sim 8$  ppm and the presence of new benzylic  $\text{CH}_2$  resonances at  $\sim 3.8$  ppm. These observations confirm that the  $\text{C}=\text{N}$  bonds have been reduced to the  $\text{CH}_2\text{-NH}$  amine linkages.

**Metal Complexes.**  $\text{N}_3\text{O}_3$  amine phenol ligands easily form aluminum, gallium and indium complexes. Chelation of the metal proceeds in an acidic medium (acetic acid is formed when the metal ion reacts with the  $\text{N}_3\text{O}_3$  amine phenols in the presence of 3–4 equiv of sodium acetate). In  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2\cdot 6.2 \text{ H}_2\text{O}$ , sodium perchlorate cocrystallizes with the complex  $[\text{Al}(\text{IIc})]$ . All complexes are soluble in dimethylsulfoxide and slightly soluble in methanol or acetone. They are stable under both basic (no metal hydroxide forms in presence of sodium hydroxide) and weakly acidic conditions. All complexes have been characterized by IR, NMR and mass spectral methods, elemental analysis and in some cases by X-ray crystallography.

All complexes show IR bands in the region 3270–3250  $\text{cm}^{-1}$ , attributable to  $\text{N}-\text{H}$  stretches of the coordinated secondary amine groups, and around 1595–1560  $\text{cm}^{-1}$  from  $\text{N}-\text{H}$  bending vibrations. Upon coordination to the metal ion, the  $\text{N}-\text{H}$  bending frequencies undergo a general bathochromic shift ( $\sim 20 \text{ cm}^{-1}$ ). The observation of broad bands at 3600–2500  $\text{cm}^{-1}$  suggests the presence of hydrogen bonding in most of these complexes. The IR spectrum of  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2$  shows split IR bands at  $\sim 1100$  and  $\sim 650 \text{ cm}^{-1}$  from the hydrogen-bonded perchlorate anions. New bands appear below 600  $\text{cm}^{-1}$  in the IR spectrum of each coordinated ligand, most likely due to  $\nu_{(\text{M}-\text{O})}$  or  $\nu_{(\text{M}-\text{N})}$ ; however, assignments of these bands are difficult.

The FAB mass spectra of all complexes were obtained in a 3-nitrobenzyl alcohol matrix in the positive ion detection mode. Results are presented in Table II. The FAB mass spectrum of  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2$  exhibits molecular ions from  $[\text{Al}(\text{IIc})+\text{H}]^+$ ,  $[\text{Al}(\text{IIc})+\text{Na}]^+$ ,  $[\text{Al}_2(\text{IIc})_2+\text{H}]^+$  and  $[\text{Al}_2(\text{IIc})_2+\text{Na}]^+$ . This is consistent with the solid state structural findings. In the spectra of complexes  $[\text{M}(\text{L})]$  ( $M = \text{Al}$ ,  $\text{Ga}$  and  $\text{In}$ ;  $L = \text{IIa}$ ), both monomeric,  $[\text{M}(\text{L}) + 1]^+$ , and the dimeric,  $[\text{M}_2(\text{L})_2 + 1]^+$ , molecular ion peaks were observed. The presence of dimeric molecular ions is probably caused by dimerization of these complexes in the mass spectrometer. In the FAB spectra of complexes  $[\text{M}(\text{L})]$  ( $M = \text{Al}$ ,  $\text{Ga}$  and  $\text{In}$ ;  $L = \text{IIb-IIId}$ ), only monomeric molecular ion peaks,  $[\text{M}(\text{L})+1]^+$ , were detected, likely because of the mass detection limits of the instrument rather than because of chemical reasons (vide infra).

**Crystal Structures.** An ORTEP drawing of  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2$  is illustrated in Figure 1; selected bond lengths and bond angles are listed in Table V. There are four  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2$  molecules and many disordered waters of hydration in the orthorhombic unit cell. Each  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2$  molecule contains 4  $[\text{Al}(\text{IIc})]$  complexes, two sodium ions and two bridging waters. The  $\{[\text{Al}(\text{IIc})]_4[\text{Na}(\text{H}_2\text{O})]_2(\text{ClO}_4)_2$  molecule is centrosymmetric with two water O atoms bridging its two halves. The  $\text{Na}^+$  ion is coordinated by two phenolate O atoms ( $\text{Na}(1)-\text{O}(1) = 2.336 \text{ \AA}$  and  $\text{Na}(1)-\text{O}(2) = 2.585 \text{ \AA}$ ) from one  $[\text{Al}(\text{IIc})]$  complex, one phenolate O ( $\text{Na}(1)-\text{O}(4) = 2.334 \text{ \AA}$ ) from the other nearest  $[\text{Al}(\text{IIc})]$  complex, and two bridging water O donor atoms ( $\text{Na}(1)-\text{O}(7) = 2.389 \text{ \AA}$  and  $\text{Na}(1)-\text{O}(7)^* = 2.347 \text{ \AA}$ ). The perchlorate

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

anion is hydrogen-bonded with O(8)---H(5) = 2.26 Å. Cavities between the hydrogen bonded ion-pairs are occupied primarily by disordered water molecules which are in partially occupied solvent sites and are involved with one another via possible weak hydrogen bonding. The only fully occupied solvent water site is O(12)—this atom is involved in a reasonably strong hydrogen bond.

The Al atom in [Al(IIc)] is bonded to all six (N<sub>3</sub>O<sub>3</sub>) donor atoms in a slightly distorted octahedral coordination geometry

with O<sub>3</sub> occupying one face of the octahedron and N<sub>3</sub> occupying the other. The Al—O and Al—N distances in each half of the {[Al(IIc)]<sub>4</sub>[Na(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>}(ClO<sub>4</sub>)<sub>2</sub> molecule are equivalent within experimental error, averaging 1.83 and 2.09 Å, respectively. These values compare well with those in [Al(HIb)]<sup>+</sup> (Al—O = 1.83 Å and Al—N = 2.08 Å), a complex in which the Al atom is also coordinated by an N<sub>3</sub>O<sub>3</sub> donor set in a distorted octahedral geometry.<sup>3</sup> The average of all six trans N—Al—O angles is 174° with the largest deviation in O(5)—Al(2)—N(6) (170°). Bond

Table IV. Final Atomic Coordinates (Fractional) and B<sub>eq</sub> (Å<sup>2</sup>)<sup>a</sup>

atom	x	y	z	B <sub>eq</sub> , Å <sup>2</sup>	occ	atom	x	y	z	B <sub>eq</sub> , Å <sup>2</sup>	occ
[Al(IIc)] <sub>4</sub> [Na(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> }(ClO <sub>4</sub> ) <sub>2</sub> ·6.22H <sub>2</sub> O											
Br(1)	0.38242(4)	0.67028(6)	0.70449(5)	7.84(7)		C(11)	0.5373(3)	0.4417(5)	0.5006(2)	3.7(4)	
Br(2)	0.50007(5)	0.11209(8)	0.43776(3)	8.78(7)		C(12)	0.4756(2)	0.3319(5)	0.5717(2)	3.4(3)	
Br(3)	0.81652(3)	0.36464(8)	0.70030(4)	7.75(6)		C(13)	0.5003(3)	0.2533(4)	0.5535(2)	3.4(3)	
Br(4)	0.56974(3)	-0.24058(6)	0.66555(4)	6.91(6)		C(14)	0.5335(2)	0.2085(5)	0.5815(2)	3.2(3)	
Br(5)	0.19140(4)	0.10179(8)	0.84451(4)	7.99(7)		C(15)	0.5560(3)	0.1365(5)	0.5651(3)	4.3(4)	
Br(6)	0.31309(5)	0.25866(9)	0.45872(4)	10.34(9)		C(16)	0.5469(3)	0.1073(5)	0.5229(3)	5.1(5)	
Cl(1)	0.2044(2)	0.0856(3)	0.5588(2)	12.0(3)		C(17)	0.5141(3)	0.1505(6)	0.4971(3)	5.2(5)	
Al(1)	0.55639(7)	0.3472(1)	0.63792(6)	2.68(9)		C(18)	0.4911(3)	0.2231(5)	0.5112(2)	4.3(4)	
Al(2)	0.38229(7)	0.0846(1)	0.67205(7)	3.1(1)		C(19)	0.6267(2)	0.4296(5)	0.5708(2)	3.6(4)	
Na(1)	0.4850(1)	0.2121(2)	0.6913(1)	3.8(1)		C(20)	0.6561(3)	0.2963(5)	0.6042(2)	3.7(4)	
O(1)	0.5035(1)	0.3544(3)	0.6757(1)	2.6(2)		C(21)	0.6778(2)	0.3258(4)	0.6479(2)	3.3(4)	
O(2)	0.5418(2)	0.2359(3)	0.6234(1)	3.0(2)		C(22)	0.6476(2)	0.3324(4)	0.6853(2)	2.8(3)	
O(3)	0.5991(1)	0.3188(3)	0.6822(1)	3.1(2)		C(23)	0.6678(3)	0.3504(5)	0.7266(3)	4.1(4)	
O(4)	0.4492(2)	0.0781(3)	0.6820(1)	3.2(2)		C(24)	0.7181(3)	0.3610(5)	0.7311(3)	5.0(5)	
O(5)	0.3701(1)	0.1263(3)	0.7278(2)	3.6(2)		C(25)	0.7473(3)	0.3547(5)	0.6941(3)	4.6(4)	
O(6)	0.3871(2)	0.1880(3)	0.6444(2)	3.5(2)		C(26)	0.7279(3)	0.3386(5)	0.6531(3)	4.2(4)	
O(7)	0.5549(2)	0.2134(3)	0.7394(1)	4.3(3)		C(27)	0.2877(3)	-0.1468(6)	0.6162(3)	6.4(5)	
O(8)	0.2426(4)	0.1238(7)	0.5789(3)	17.1(8)		C(28)	0.3187(3)	-0.0735(5)	0.6344(3)	4.4(4)	
O(9)	0.1832(6)	0.130(1)	0.5279(5)	29(2)		C(29)	0.3528(3)	-0.1075(5)	0.6706(3)	4.2(4)	
O(10)	0.1717(5)	0.052(2)	0.5909(7)	35(2)		C(30)	0.4148(3)	-0.0675(5)	0.7265(2)	3.9(4)	
O(11)	0.226(1)	0.014(1)	0.5396(7)	32(2)		C(31)	0.4607(2)	-0.0675(5)	0.6993(2)	3.1(3)	
O(12)	0.0626(3)	0.0485(7)	0.5798(2)	11.0(5)		C(32)	0.4774(2)	0.0071(5)	0.6808(2)	2.9(3)	
O(13)	0.1181(7)	0.231(1)	0.5042(5)	21(2)	0.59	C(33)	0.5233(2)	0.0102(4)	0.6608(2)	3.3(3)	
O(13A)	0.055(1)	0.160(2)	0.577(1)	22(3)	0.41	C(34)	0.5510(2)	-0.0625(5)	0.6569(2)	3.5(4)	
O(14)	0.297(1)	-0.010(3)	0.450(1)	20(1)	0.34	C(35)	0.5332(2)	-0.1384(5)	0.6730(2)	3.5(4)	
O(14A)	0.322(1)	-0.177(3)	0.495(1)	21(1)	0.33	C(36)	0.4880(3)	-0.1413(5)	0.6943(2)	3.7(4)	
O(15)	0.695(1)	0.070(2)	0.524(1)	20(1)	0.44	C(37)	0.2842(3)	-0.0064(5)	0.6545(3)	4.4(4)	
N(1)	0.5763(2)	0.4740(3)	0.6491(2)	2.7(3)		C(38)	0.2783(3)	0.1394(5)	0.6856(3)	4.5(4)	
N(2)	0.5121(2)	0.3956(3)	0.5877(2)	2.7(2)		C(39)	0.2831(2)	0.1222(5)	0.7344(3)	3.6(4)	
N(3)	0.6122(2)	0.3468(3)	0.5905(2)	2.8(3)		C(40)	0.3301(3)	0.1185(5)	0.7539(3)	3.8(4)	
N(4)	0.3714(2)	-0.0382(4)	0.6996(2)	3.3(3)		C(41)	0.3345(3)	0.1097(5)	0.7989(3)	4.2(4)	
N(5)	0.3077(2)	0.0809(4)	0.6575(2)	3.7(3)		C(42)	0.2938(3)	0.1033(5)	0.8267(3)	5.2(5)	
N(6)	0.3909(2)	0.0174(4)	0.6126(2)	3.4(3)		C(43)	0.2486(3)	0.1065(5)	0.8076(3)	4.9(4)	
C(1)	0.5948(3)	0.5591(5)	0.5320(3)	5.2(5)		C(44)	0.2422(3)	0.1145(5)	0.7626(3)	4.8(5)	
C(2)	0.5826(3)	0.4905(5)	0.5664(2)	3.5(4)		C(45)	0.3489(3)	-0.0341(5)	0.5961(2)	4.2(4)	
C(3)	0.5720(2)	0.5341(4)	0.6108(2)	3.2(3)		C(46)	0.4123(3)	0.0720(5)	0.5771(2)	4.2(4)	
C(4)	0.5541(2)	0.5079(4)	0.6910(2)	3.3(3)		C(47)	0.3816(3)	0.1475(5)	0.5683(3)	3.8(4)	
C(5)	0.4987(2)	0.5040(5)	0.6894(2)	2.8(3)		C(48)	0.3717(2)	0.2044(5)	0.6029(3)	3.6(4)	
C(6)	0.4765(2)	0.4245(4)	0.6827(2)	2.8(3)		C(49)	0.3462(3)	0.2796(5)	0.5938(3)	4.6(4)	
C(7)	0.4248(2)	0.4206(5)	0.6827(2)	3.5(4)		C(50)	0.3296(3)	0.2955(6)	0.5503(4)	6.1(6)	
C(8)	0.3970(2)	0.4939(5)	0.6889(3)	4.1(4)		C(51)	0.3386(3)	0.2379(8)	0.5168(3)	6.3(6)	
C(9)	0.4200(3)	0.5694(5)	0.6954(3)	3.8(4)		C(52)	0.3644(3)	0.1632(6)	0.5254(3)	5.1(5)	
C(10)	0.4705(3)	0.5758(4)	0.6959(2)	3.5(4)							
[Ga(IIa)]·4.35H <sub>2</sub> O											
Ga(1)	0.38391(1)	0.42029(4)	0.37898(2)	3.44(1)		C(6)	0.4510(1)	0.2410(3)	0.3891(2)	3.7(1)	
O(1)	0.44383(7)	0.3353(2)	0.4288(1)	3.95(8)		C(7)	0.4622(1)	0.1187(4)	0.4190(2)	4.8(1)	
O(2)	0.35090(7)	0.2649(2)	0.3345(1)	3.96(9)		C(8)	0.4693(1)	0.0233(4)	0.3776(3)	5.8(2)	
O(3)	0.37465(8)	0.4096(2)	0.4687(1)	4.7(1)		C(9)	0.4648(2)	0.0471(4)	0.3056(3)	6.0(2)	
O(4)	0.49561(9)	0.3270(3)	0.5871(1)	6.2(1)		C(10)	0.4544(1)	0.1684(4)	0.2761(2)	5.1(2)	
O(5)	0.3577(5)	0.173(1)	0.5055(7)	15.8(6)	0.53	C(11)	0.3142(1)	0.6100(3)	0.2582(2)	4.5(1)	
O(6)	0.3593(2)	0.0349(5)	0.4060(4)	12.2(4)	0.72	C(12)	0.2767(1)	0.4363(4)	0.2929(2)	4.6(1)	
O(7)	0.434(1)	0.258(4)	0.643(2)	11(1)	0.19	C(13)	0.2767(1)	0.3394(3)	0.2371(2)	4.1(1)	
O(8)	0.4025(8)	0.204(2)	0.578(1)	15(1)	0.39	C(14)	0.3149(1)	0.2552(3)	0.2630(2)	3.8(1)	
O(9)	0.2788(7)	0.154(2)	0.461(1)	40(1)	0.75	C(15)	0.3144(1)	0.1607(3)	0.2127(2)	4.6(1)	
O(10)	0.4753(9)	0.272(2)	0.703(1)	15(1)	0.27	C(16)	0.2764(2)	0.1510(4)	0.1389(2)	5.8(2)	
O(11)	0.394(1)	0.083(5)	0.583(2)	21(2)	0.25	C(17)	0.2387(2)	0.2351(5)	0.1134(2)	6.1(2)	
O(12)	0.4440(8)	0.175(3)	0.648(1)	10(1)	0.24	C(18)	0.2394(1)	0.3287(4)	0.1622(2)	5.2(2)	
N(1)	0.39435(9)	0.4544(2)	0.2786(1)	3.4(1)		C(19)	0.3895(1)	0.7064(3)	0.3637(2)	4.5(1)	
N(2)	0.31897(9)	0.5213(3)	0.3205(1)	3.8(1)		C(20)	0.4357(1)	0.6226(4)	0.4966(2)	4.7(1)	
N(3)	0.41648(9)	0.5970(3)	0.4123(1)	3.8(1)		C(21)	0.3980(1)	0.6184(4)	0.5210(2)	4.6(1)	
C(1)	0.3498(2)	0.7971(4)	0.2303(2)	5.9(2)		C(22)	0.3701(1)	0.5101(4)	0.5071(2)	4.4(1)	
C(2)	0.3612(1)	0.6732(3)	0.2774(2)	4.2(1)		C(23)	0.3371(1)	0.5053(4)	0.5346(2)	5.3(2)	
C(3)	0.3905(1)	0.5904(3)	0.2528(2)	4.1(1)		C(24)	0.3328(1)	0.6079(5)	0.5757(2)	5.8(2)	
C(4)	0.4400(1)	0.4009(3)	0.2886(2)	4.1(1)		C(25)	0.3596(2)	0.7125(5)	0.5887(2)	6.4(2)	
C(5)	0.4479(1)	0.2664(3)	0.3172(2)	3.9(1)		C(26)	0.3926(1)	0.7188(4)	0.5617(2)	5.7(2)	

Table IV (Continued)

atom	x	y	z	$B_{eq}, \text{\AA}^2$	occ	atom	x	y	z	$B_{eq}, \text{\AA}^2$	occ
[In(IIa)]·4.57H <sub>2</sub> O											
In(1)	0.38559(1)	0.39876(3)	0.39062(2)	3.84(1)		C(7)	0.4622(2)	0.0978(5)	0.4144(3)	5.8(2)	
O(1)	0.4499(1)	0.3084(3)	0.4368(2)	4.8(1)		C(8)	0.4649(2)	0.0073(6)	0.3663(4)	6.9(3)	
O(2)	0.3480(1)	0.2330(3)	0.3459(2)	5.1(1)		C(9)	0.4586(2)	0.0377(6)	0.2930(4)	7.0(3)	
O(3)	0.3802(1)	0.4007(3)	0.4939(2)	5.9(2)		C(10)	0.4501(2)	0.1593(5)	0.2689(3)	5.7(2)	
O(4)	0.5033(1)	0.3319(4)	0.5909(2)	6.7(2)		C(11)	0.3136(2)	0.5837(4)	0.2613(3)	4.7(2)	
O(5)	0.301(1)	0.129(3)	0.470(2)	24(1)	0.41	C(12)	0.2761(2)	0.4121(5)	0.2952(3)	5.2(2)	
O(6)	0.3542(4)	0.029(1)	0.4332(7)	28.2(9)		C(13)	0.2785(2)	0.3141(5)	0.2432(3)	4.8(2)	
O(7)	0.4207(4)	0.229(1)	0.6160(6)	22.5(8)		C(14)	0.3147(2)	0.2282(5)	0.2721(3)	4.6(2)	
O(8)	0.347(2)	0.108(4)	0.536(3)	21(2)	0.25	C(15)	0.3155(2)	0.1341(5)	0.2230(4)	6.3(3)	
O(9)	0.4880(9)	0.311(2)	0.720(1)	20(1)	0.47	C(16)	0.2806(3)	0.1250(7)	0.1478(4)	8.1(4)	
O(10)	0.421(1)	0.030(3)	0.579(2)	26(2)	0.44	C(17)	0.2448(3)	0.2073(8)	0.1193(4)	8.2(4)	
N(1)	0.3947(1)	0.4384(2)	0.2807(2)	3.8(1)		C(18)	0.2439(2)	0.3027(6)	0.1663(3)	6.5(3)	
N(2)	0.3160(1)	0.4997(4)	0.3235(2)	4.3(1)		C(19)	0.3852(2)	0.6910(4)	0.3663(3)	4.9(2)	
N(3)	0.4153(1)	0.5928(3)	0.4198(2)	4.3(1)		C(20)	0.4321(2)	0.6244(5)	0.5031(3)	5.5(2)	
C(1)	0.3471(2)	0.7695(5)	0.2306(3)	6.0(2)		C(21)	0.3947(2)	0.6191(5)	0.5268(3)	5.6(2)	
C(2)	0.3593(2)	0.6505(4)	0.2806(3)	4.3(2)		C(22)	0.3711(2)	0.5081(6)	0.5217(2)	5.6(2)	
C(3)	0.3904(2)	0.5723(4)	0.2581(2)	4.2(2)		C(23)	0.3371(2)	0.5064(7)	0.5465(3)	7.0(3)	
C(4)	0.4401(2)	0.3856(5)	0.2912(3)	4.6(2)		C(24)	0.3285(2)	0.6151(8)	0.5791(3)	7.8(3)	
C(5)	0.4472(2)	0.2527(4)	0.3165(3)	4.4(2)		C(25)	0.3519(3)	0.7197(8)	0.5842(4)	8.5(4)	
C(6)	0.4531(1)	0.2214(4)	0.3896(3)	4.3(2)		C(26)	0.3844(2)	0.7239(6)	0.5581(3)	7.3(3)	

$${}^a B_{eq} = (8/3)\pi^2 \sum \sum U_{ij} a_i^* a_j^* (a_i a_j).$$

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) in [Al(IIc)]<sub>4</sub>[Na(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·6.2H<sub>2</sub>O

Bond Lengths			
Al(1)–O(1)	1.838(4)	Al(1)–N(1)	2.090(6)
Al(1)–O(2)	1.842(5)	Al(1)–N(2)	2.075(5)
Al(1)–O(3)	1.820(4)	Al(1)–N(3)	2.083(5)
Al(2)–O(4)	1.850(5)	Al(1)–N(4)	2.118(6)
Al(2)–O(5)	1.827(5)	Al(1)–N(5)	2.077(6)
Al(2)–O(6)	1.827(5)	Al(1)–N(6)	2.085(6)
Na(1)–O(1)	2.336(5)	Na(1)–O(7)	2.389(5)
Na(1)–O(2)	2.585(5)	Na(1)–O(7) <sup>a</sup>	2.347(5)
Na(1)–O(4)	2.334(5)		
Bond Angles			
O(1)–Al(1)–O(2)	92.1(2)	O(4)–Al(2)–O(5)	92.9(2)
O(1)–Al(1)–O(3)	93.7(2)	O(4)–Al(2)–O(6)	92.9(2)
O(1)–Al(1)–N(1)	92.6(2)	O(4)–Al(2)–N(4)	91.5(2)
O(1)–Al(1)–N(2)	88.3(2)	O(4)–Al(2)–N(5)	174.4(2)
O(1)–Al(1)–N(3)	174.1(2)	O(4)–Al(2)–N(6)	89.9(2)
O(2)–Al(1)–O(3)	94.5(2)	O(5)–Al(2)–O(6)	96.4(2)
O(2)–Al(1)–N(1)	175.0(2)	O(5)–Al(2)–N(4)	86.7(2)
O(2)–Al(1)–N(2)	92.9(2)	O(5)–Al(2)–N(5)	91.5(2)
O(2)–Al(1)–N(3)	89.6(2)	O(5)–Al(2)–N(6)	170.0(2)
O(3)–Al(1)–N(1)	87.1(2)	O(6)–Al(2)–N(4)	174.5(2)
O(3)–Al(1)–N(2)	172.3(2)	O(6)–Al(2)–N(5)	90.0(2)
O(3)–Al(1)–N(3)	91.8(2)	O(6)–Al(2)–N(6)	93.0(2)
N(1)–Al(1)–N(2)	85.4(2)	N(4)–Al(2)–N(5)	85.4(2)
N(1)–Al(1)–N(3)	85.5(2)	N(4)–Al(2)–N(6)	83.7(2)
N(2)–Al(1)–N(3)	85.9(2)	N(5)–Al(2)–N(6)	85.2(2)
O(1)–Na(1)–O(2)	64.9(1)	O(2)–Na(1)–O(7)	89.9(2)
O(1)–Na(1)–O(4)	157.9(2)	O(2)–Na(1)–O(7) <sup>a</sup>	167.0(2)
O(1)–Na(1)–O(7)	86.7(2)	O(4)–Na(1)–O(7)	114.4(2)
O(1)–Na(1)–O(7) <sup>a</sup>	105.6(2)	O(4)–Na(1)–O(7) <sup>a</sup>	85.4(2)
O(2)–Na(1)–O(4)	106.6(2)	O(7)–Na(1)–O(7) <sup>a</sup>	80.4(2)
C(1)–C(2)–C(3)	108.5(6)	C(27)–C(28)–C(29)	109.1(6)
C(1)–C(2)–C(11)	108.6(6)	C(27)–C(28)–C(37)	108.6(6)
C(1)–C(2)–C(19)	109.0(6)	C(27)–C(28)–C(45)	109.3(6)
C(3)–C(2)–C(11)	110.1(6)	C(29)–C(28)–C(37)	109.4(7)
C(3)–C(2)–C(19)	110.5(6)	C(29)–C(28)–C(45)	110.3(6)
C(11)–C(2)–C(19)	110.2(6)	C(37)–C(28)–C(45)	110.2(6)
N(1)–C(3)–C(2)	112.0(5)	N(4)–C(29)–C(28)	111.7(6)
N(2)–C(11)–C(2)	112.5(5)	N(5)–C(37)–C(28)	112.5(6)
N(3)–C(19)–C(2)	111.8(5)	N(6)–C(45)–C(28)	112.2(6)

<sup>a</sup> Symmetry operation: 1 – x, y, 3/2 – z (here and elsewhere).

angles between the apical methyl carbon atom C(1) and the three chelating arms (Chart I,  $\angle = 108.9^\circ$  within  $0.6^\circ$ ) suffer little deviation from  $109.5^\circ$ . The bond angles between the three

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) in [Ga(IIa)]·4.4H<sub>2</sub>O

Bond Lengths			
Ga(1)–O(1)	1.916(2)	Ga(1)–N(1)	2.180(3)
Ga(1)–O(2)	1.922(2)	Ga(1)–N(2)	2.127(3)
Ga(1)–O(3)	1.923(2)	Ga(1)–N(3)	2.086(3)
Bond Angles			
O(1)–Ga(1)–O(2)	92.0(1)	O(2)–Ga(1)–N(3)	172.5(1)
O(1)–Ga(1)–O(3)	93.5(1)	O(3)–Ga(1)–N(1)	173.9(1)
O(1)–Ga(1)–N(1)	89.4(1)	O(3)–Ga(1)–N(2)	89.1(1)
O(1)–Ga(1)–N(2)	176.8(1)	O(3)–Ga(1)–N(3)	92.2(1)
O(1)–Ga(1)–N(3)	91.5(1)	N(1)–Ga(1)–N(2)	87.9(1)
O(2)–Ga(1)–O(3)	94.2(1)	N(1)–Ga(1)–N(3)	82.3(1)
O(2)–Ga(1)–N(1)	91.1(1)	N(2)–Ga(1)–N(3)	86.4(1)
O(2)–Ga(1)–N(2)	89.8(1)		
C(1)–C(2)–C(3)	107.6(1)	C(3)–C(2)–C(11)	111.0(3)
C(1)–C(2)–C(11)	107.4(1)	C(3)–C(2)–C(19)	110.7(3)
C(1)–C(2)–C(19)	108.3(1)	C(11)–C(2)–C(19)	111.6(3)
N(1)–C(3)–C(2)	113.9(3)	N(3)–C(19)–C(2)	112.9(3)
N(2)–C(11)–C(2)	111.7(3)		

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) in [In(IIa)]·4.6H<sub>2</sub>O

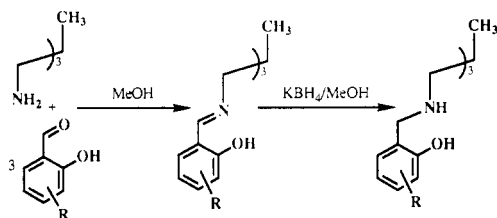
Bond Lengths			
In(1)–O(1)	2.098(3)	In(1)–N(1)	2.330(3)
In(1)–O(2)	2.107(3)	In(1)–N(2)	2.296(4)
In(1)–O(3)	2.096(3)	In(1)–N(3)	2.257(4)
Bond Angles			
O(1)–In(1)–O(2)	93.4(1)	O(2)–In(1)–N(3)	169.6(1)
O(1)–In(1)–O(3)	96.4(1)	O(3)–In(1)–N(1)	168.7(1)
O(1)–In(1)–N(1)	86.9(1)	O(3)–In(1)–N(2)	92.0(1)
O(1)–In(1)–N(2)	171.6(1)	O(3)–In(1)–N(3)	88.2(1)
O(1)–In(1)–N(3)	95.3(1)	N(1)–In(1)–N(2)	84.8(1)
O(2)–In(1)–O(3)	96.3(1)	N(1)–In(1)–N(3)	80.6(1)
O(2)–In(1)–N(1)	94.4(1)	N(2)–In(1)–N(3)	84.3(1)
O(2)–In(1)–N(2)	86.2(1)		
C(1)–C(2)–C(3)	106.5(4)	C(3)–C(2)–C(11)	111.8(4)
C(1)–C(2)–C(11)	107.3(4)	C(3)–C(2)–C(19)	111.2(4)
C(1)–C(2)–C(19)	107.3(4)	C(11)–C(2)–C(19)	112.3(4)
N(1)–C(3)–C(2)	115.4(4)	N(3)–C(19)–C(2)	114.0(4)
N(2)–C(11)–C(2)	114.2(4)		

chelating arms ( $B = 110.1^\circ$  within  $0.6^\circ$ ) also show no significant deviation from  $T_d$  values. Furthermore, the present example represents one of few structurally characterized aluminum complexes containing only hexadentate ligands.<sup>3,24–26</sup>

(24) Polynova, T. N.; Bel'skaya, N. P.; Tyurk de Garia Banas, D.; Porai-Koshits, M. A.; Martynenko, L. I. *Zh. Strukt. Khim.* 1970, 11, 164.

(25) van der Helm, D.; Baker, J. R.; Lohry, R. A.; Ekstrand, J. D. *Acta Crystallogr.* 1981, B37, 323.

## Scheme I

Table VIII.  $^1\text{H}$  NMR Data for Schiff Bases ( $\delta$  in ppm from TMS,  $\text{CDCl}_3$ )

$R_1 = R_2 = \text{H}$	$R_1 = \text{H}, R_2 = \text{Cl}$	$R_1 = \text{H}, R_2 = \text{Br}$	$R_1 = R_2 = \text{Cl}$	assignment
1.16 (s, 3H)	1.08 (s, 3H)	1.08 (s, 3H)	1.06 (s, 3H)	H1
3.62 (s, 6H)	3.62 (s, 6H)	3.62 (s, 6H)	3.70 (s, 6H)	H3
8.38 (s, 3H)	8.30 (s, 3H)	8.30 (s, 3H)	8.36 (s, 3H)	H4
7.00 (d, 3H)	6.90 (d, 3H)	6.90 (d, 3H)		H7
7.38 (t, 3H)	7.38 (d, 3H)	7.40 (d, 3H)	7.40 (s, 3H)	H8
6.90 (t, 3H)				H9
7.25 (d, 3H)	7.20 (s, 3H)	7.20 (s, 3H)	7.15 (s, 3H)	H10
13.4 (s, 3H)	13.2 (s, 3H)	13.2 (s, 3H)	14.1 (s, 3H)	OH

Table IX.  $^1\text{H}$  NMR Data for Amine Phenols ( $\delta$  in ppm from TMS,  $\text{CDCl}_3$ )

$R_1 = R_2 = \text{H}$	$R_1 = \text{H}, R_2 = \text{Cl}$	$R_1 = \text{H}, R_2 = \text{Br}$	$R_1 = R_2 = \text{Cl}$	assignment
0.94 (s, 3H)	0.95 (s, 3H)	0.95 (s, 3H)	0.94 (s, 3H)	H1
2.40 (s, 6H)	2.50 (s, 6H)	2.50 (s, 6H)	2.45 (s, 6H)	H3
3.82 (s, 6H)	3.90 (s, 3H)	3.90 (s, 6H)	3.86 (s, 6H)	H4
6.80 (d, 3H)	6.70 (d, 3H)	6.65 (d, 3H)		H7
7.05 (t, 3H)	7.10 (d, 3H)	7.25 (d, 3H)	7.18 (s, 3H)	H8
6.70 (t, 3H)				H9
6.90 (d, 3H)	7.00 (d, 3H)	7.10 (s, 3H)	6.85 (s, 3H)	H10

An ORTEP drawing of  $[\text{Ga}(\text{IIa})]\cdot\text{H}_2\text{O}$  is illustrated in Figure 2. The selected bond lengths and bond angles are listed in Table VI. In the monoclinic unit cell there are eight  $[\text{Ga}(\text{IIa})]\cdot\text{H}_2\text{O}$  molecules (four pairs of  $\Delta$  and  $\Delta$  enantiomers) and many disordered waters of hydration. The water molecule in  $[\text{Ga}(\text{IIa})]\cdot\text{H}_2\text{O}$  is hydrogen bonded to a phenolate oxygen atom ( $\text{O}(1)\cdots\text{H}(1) = 1.90 \text{ \AA}$ ). The complex is neutral with a triply deprotonated  $\text{N}_3\text{O}_3$  amine phenol ligand completely encapsulating the  $\text{Ga}^{3+}$  ion. Each  $\text{N}_3$  and  $\text{O}_3$  donor set coordinates to the  $\text{Ga}^{3+}$  ion in a facial manner to form a slightly distorted octahedral coordination geometry. The distortion of the coordination sphere is most evident in the compression of  $\text{N-Ga-N}$  angles (average  $\text{N-Ga-N} = 85.5^\circ$ ) and expansion in the  $\text{O-Ga-O}$  angles (average  $\text{O-Ga-O} = 93.2^\circ$ ) from  $90^\circ$ . As a result, the three trans  $\text{N-Ga-O}$  angles are  $176.8, 172.5$  and  $173.9^\circ$  for  $\text{O}(1)-\text{Ga}(1)-\text{N}(2)$ ,  $\text{O}(2)-\text{Ga}(1)-\text{N}(3)$  and  $\text{O}(3)-\text{Ga}(1)-\text{N}(1)$ , respectively. The  $\text{Ga-O}$  distances are equivalent within the experimental error averaging  $1.92 \text{ \AA}$  while the  $\text{Ga-N}$  bond lengths are  $2.180, 2.127$  and  $2.086$

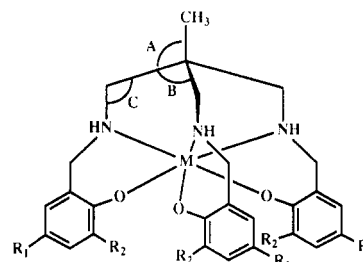
(26) Moise, F.; Pennington, W. F.; Robinson, G. H. *J. Coord. Chem.* 1991, 24, 93.Table X.  $^{13}\text{C}$  NMR Data for Schiff Bases ( $\delta$  in ppm from TMS,  $\text{CDCl}_3$ )

$R_1 = R_2 = \text{H}$	$R_1 = \text{H}, R_2 = \text{Cl}$	$R_1 = \text{H}, R_2 = \text{Br}$	$R_1 = R_2 = \text{Cl}$	assignment
20.8	20.8	20.8	20.7	C1
40.2	40.4	40.2	40.1	C2
65.0	65.6	65.0	64.3	C3
166.6	166.5	165.5	165.5	C4
118.7	119.5	119.9	119.4	C5
161.0	159.6	160.1	156.0	C6
116.9	118.9	119.0	123.3	C7
132.2	132.6	135.4	132.6	C8
118.8	123.8	110.4	122.7	C9
131.5	131.0	133.7	129.3	C10

Table XI.  $^{13}\text{C}$  NMR Data for Amine Phenols ( $\delta$  in ppm from TMS,  $\text{CDCl}_3$ )

$R_1 = R_2 = \text{H}$	$R_1 = \text{H}, R_2 = \text{Cl}$	$R_1 = \text{H}, R_2 = \text{Br}$	$R_1 = R_2 = \text{Cl}$	assignment
20.8	20.8	20.8	20.7	C1
38.1	38.1	38.0	40.1	C2
54.9	53.5	53.5	53.5	C3
53.0	52.6	52.4	52.5	C4
122.4	124.1	124.1	121.6	C5
157.6	156.1	156.7	152.1	C6
116.2	117.5	118.0	124.0	C7
129.0	128.9	131.4	127.1	C8
119.4	123.5	111.2	124.3	C9
128.8	128.5	131.8	128.9	C10

## Chart I



M	A ( $^\circ$ )	B ( $^\circ$ )	C ( $^\circ$ )
Al	108.9	110.1	112.1
Ga	107.8	111.1	112.8
In	107.0	111.8	114.5

$\text{\AA}$ , for  $\text{Ga}(1)-\text{N}(1)$ ,  $\text{Ga}(1)-\text{N}(2)$  and  $\text{Ga}(1)-\text{N}(3)$ , respectively, averaging  $2.13 \text{ \AA}$ . These values fall in the ranges  $1.900\text{--}1.996 \text{ \AA}$  for  $\text{Ga-O}$  and  $2.097\text{--}2.221 \text{ \AA}$  for  $\text{Ga-N}$  found in  $[\text{Ga}(\text{HCl})]^+$ ,<sup>3</sup>  $[\text{Ga}(\text{TX-TACN})\text{H}]^+$ ,<sup>5,6</sup>  $\text{Ga}[(5\text{-MeO-sal})\text{tame}]$ ,<sup>12</sup> and in  $\text{Ga-N}_3\text{O}_3$  and  $\text{Ga-N}_3\text{S}_3$  complexes.<sup>6</sup> Bond angles between the carbon atom C(1) and the three chelating arms ( $A = 107.8^\circ$ , within  $0.1^\circ$ ) show a slight lowering from  $109.5^\circ$ . Conversely, bond angles between the three chelating arms ( $B = 111.1^\circ$ , within  $0.3^\circ$ ) are slightly increased from  $T_d$  values.

$[\text{In}(\text{IIa})]\cdot\text{H}_2\text{O}$  and  $[\text{Ga}(\text{IIa})]\cdot\text{H}_2\text{O}$  are isomorphous. The water

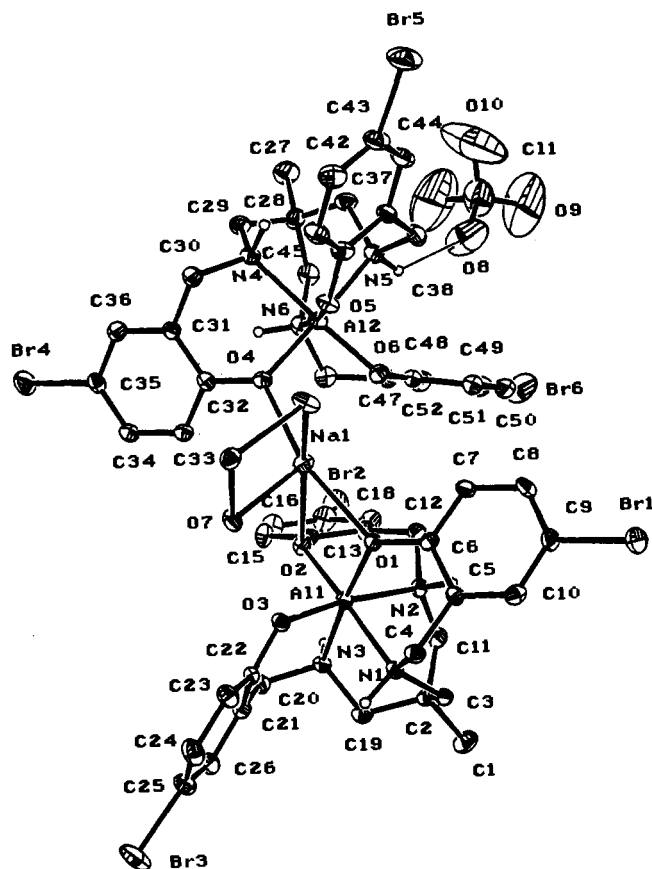


Figure 1. ORTEP drawing of the asymmetric unit  $\{[Al(IIc)]_2[Na(H_2O)]\} \cdot ClO_4$  in  $\{[Al(IIc)]_4[Na(H_2O)]_2\}(ClO_4)_2$ .

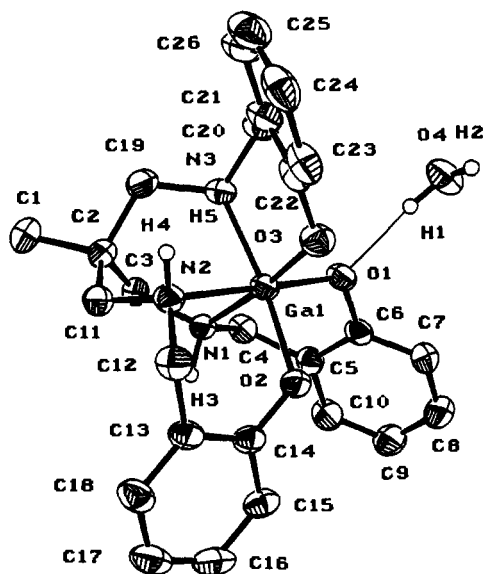
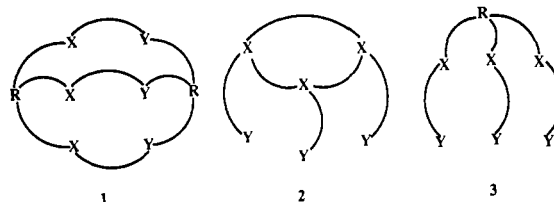


Figure 2. ORTEP drawing of the  $[Ga(IIa)] \cdot H_2O$  unit in  $[Ga(IIa)] \cdot 4.4H_2O$ . The indium complex is isostructural.

molecule in  $[In(IIa)] \cdot H_2O$  is hydrogen bonded with a phenolate oxygen atom ( $O(1) \cdots H(1) = 1.90 \text{ \AA}$ ). The complex is neutral with  $In^{3+}$  being encapsulated by a triply deprotonated  $N_3O_3$  amine phenol ligand in a slightly distorted octahedral geometry with  $O_3$  and  $N_3$  donors occupying two faces of the octahedron. The  $In-O$  distances in  $[In(IIa)] \cdot H_2O$  are 2.098, 2.107 and 2.096  $\text{\AA}$  for  $In(1)-O(1)$ ,  $In(1)-O(2)$  and  $In(1)-O(3)$  respectively, averaging 2.10  $\text{\AA}$  while the  $In-N$  bond lengths are 2.330, 2.296, 2.257  $\text{\AA}$  for  $In(1)-N(1)$ ,  $In(1)-N(2)$  and  $In(1)-N(3)$ , respectively, averaging 2.29  $\text{\AA}$ . Both  $In-O$  and  $In-N$  bond lengths are shorter than those (average:  $In-O = 2.169 \text{ \AA}$  and  $In-N(\text{secondary amine}) = 2.330$

## Scheme II



$\text{\AA}$ ) found in  $Na[In(IIa)](NO_3)(H_2O)(C_2H_5OH)$ , a complex in which the  $In$  atom is coordinated by  $N_4O_3$  donors.<sup>3</sup> Three trans  $N-In-O$  angles are 171.6, 169.6 and 168.7° for  $O(1)-In(1)-N(2)$ ,  $O(2)-In(1)-N(3)$  and  $O(3)-In(1)-N(1)$ , respectively. The average of the  $O-In-O$  angles is 95.4° while that of  $N-In-N$  bond angles is 83.2°. Compared with those in  $[Ga(IIa)] \cdot H_2O$ , there are no significant changes in bond angles between the apical carbon atom and the three chelate-bearing arms ( $A = 107.0^\circ$  within 0.4°) and those at the quaternary carbon atom between chelate arms ( $B = 111.8^\circ$  within 0.4°). However, the bond angle  $C$  in each chelating arm is slightly expanded from the  $Ga$  complex ( $C = 112.8^\circ$  within 0.3°) to the  $In$  complex ( $C = 114.5^\circ$  within 0.4°).

**Metal Complex NMR.** The  $^1H$  NMR spectral results of the complexes,  $\{[Al(IIc)]_4[Na(H_2O)]_2(ClO_4)_2\}$  and  $[M(L)]$  ( $M = Al, Ga$  and  $In$ ,  $L = IIa-IId$ ), in  $DMSO-d_6$  are shown in Table XII. The spectra are very similar to each other except for those resonance signals from aromatic hydrogens in the region 6.5–7.5 ppm; only that of the gallium complex of  $H_3IIa$  is discussed as a representative example. As for the ligands, the spectral assignments for the complexes were made based on  $^1H-^1H$  COSY,  $^1H-^{13}C$  hetero-correlation and APT (attached proton test) spectra. No specific assignments were made for the resonance signals from hydrogens on  $C3$  and  $C4$  of the coordinated amine phenol ligand.

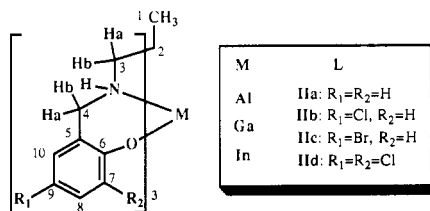
In the uncoordinated amine phenol  $H_3IIa$ , the two hydrogen atoms on  $C4$  and on  $C3$  are equivalent. Thus, in the  $^1H$  spectrum of  $H_3IIa$ , there appears only a singlet at 3.82 ppm from hydrogens on  $C4$ , and a singlet at 2.40 ppm from those on  $C3$ . Upon coordination to the metal ion ( $Ga^{3+}$ ), the singlet at 3.82 ppm appears as two broad doublets at 3.18 and 4.10 ppm. The singlet at 2.4 ppm becomes a multiplet at 2.70 ppm. These changes point to the non-equivalency of the hydrogens at  $C3$  and  $C4$  in the complex. The signals in the aromatic region remain relatively unchanged with only slight shifts upon coordination. These observations clearly demonstrate that the metal complex in  $DMSO$  is highly symmetric; all three chelating arms are equivalent. The nature of the  $C_3$  symmetry of the complex in solution is consistent with the solid state structural findings and is also supported by  $^{13}C$  NMR data, which show only 10 distinct resonance signals in the  $^{13}C$  spectrum of  $[Ga(IIa)]$ .

Since all the complexes have similar structures, the variable temperature (21–150 °C)  $^1H$  NMR were obtained only for complexes  $[M(IIa)]$  ( $M = Al, Ga$  and  $In$ ) in order to examine their fluxionalities in  $DMSO$  solution. There are no significant changes in the spectral parameters except for some minor shifts for all hydrogen signals. These shifts are probably caused by the thermal vibrations of the coordinated ligand framework. These observations clearly show that aluminum, gallium and indium complexes remain very rigid in  $DMSO$  solution.

**Concluding Remarks.** High stability is an important prerequisite for new potential  $^{67}Ga$ - or  $^{111}In$ -complex radiopharmaceuticals in order to resist acid or cation mediated decomplexation and subsequent exchange with serum proteins such as transferrin.<sup>27</sup> Polydentate ligands with intrinsically three-dimensional cavities are of particular interest in this regard, because of the high stability of their metal complexes, the substantial selectivity in their binding by enforcing a specific spatial arrangement of

(27) Harris, W. R.; Pecoraro, V. L. *Biochemistry* 1983, 22, 292.



**Table XII.**  $^1\text{H}$  NMR (200 MHz) Data for Coordinated Amine Phenols in  $[\text{M}(\text{L})]$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ;  $\text{L} = \text{IIa-IId}$ ) in  $\text{DMSO-}d_6$ ,  $\delta$  in ppm from TMS<sup>a</sup>

complex	H1	H3a and H3b	H4a and H4b	H7	H8	H9	H10	N-H
[Al(IIa)]	0.58(s)	2.70 (m), 2.90 (m)	3.60 (d), 3.80 (d)	6.35 (d)	7.00 (t)	6.45 (t)	6.90 (d)	3.70 (bs)
[Al(IIb)]	0.58(s)	2.50 (m)	3.08 (d), 3.95 (d)	6.46 (d)	7.08 (d)		7.02 (s)	3.30 (bs)
[Al(IIc)]	0.58(s)	2.54 (m)	3.08 (d), 3.96 (d)	6.40 (d)	7.18 (d)		7.14 (s)	3.30 (bs)
[Al(IId)]	0.60(s)	2.50 (m)	3.10 (d), 4.18 (d)		7.30 (s)		7.06 (s)	3.50 (bs)
[Ga(IIa)]	0.56(s)	2.70 (m)	3.18 (d), 4.10 (d)	6.48 (d)	7.10 (t)	6.50 (t)	6.95 (d)	4.45 (bs)
[Ga(IIb)]	0.58(s)	2.65 (m)	3.20 (d), 3.95 (d)	6.40 (d)	7.06 (d)		7.00 (s)	3.55 (bs)
[Ga(IIc)]	0.58(s)	2.65 (m)	3.20 (d), 3.95 (d)	6.38 (d)	7.12 (s)		7.10 (s)	3.58 (bs)
[Ga(IId)]	0.58(s)	2.60 (m)	3.24 (d), 4.10 (d)		7.30 (s)		7.08 (s)	3.80 (bs)
[In(IIa)]	0.58(s)	2.60 (m)	3.10 (d), 4.10 (d)	6.50 (d)	7.10 (t)	6.54 (t)	7.00 (d)	3.26 (bs)
[In(IIb)]	0.60(s)	2.64 (m), 2.80 (m)	3.56 (d), 3.78 (d)	6.30 (d)	7.02 (d)		6.98 (s)	4.00 (bs)
[In(IIc)]	0.60(s)	2.60 (m), 2.80 (m)	3.56 (d), 3.75 (d)	6.28 (d)	7.12 (d)		7.08 (s)	4.05 (bs)
[In(IId)]	0.60(s)	2.70 (m)	3.50 (d), 3.88 (d)		7.28 (s)		7.00 (s)	4.18 (bs)

<sup>a</sup>  $^3J_{\text{HH}} = 6.8\text{--}7.0$  Hz;  $^2J_{\text{HH}} = 12.0\text{--}13.0$  Hz.

donor atoms or by introducing different donor atoms. Several ligand systems (Scheme II) can be envisioned for building polydentate ligands with three-dimensional cavities. Since the discovery of crown ethers by Pedersen,<sup>28</sup> many cryptands (**1**)<sup>29–31</sup> and macrocycles with different pendent arms (**2**)<sup>5–9,32,33</sup> have been synthesized and their coordination chemistries have been extensively investigated.<sup>29–33</sup> For harder trivalent metal ions, we have found **3** to be easier to synthesize than **1** or **2**. Synthesis of tripodal ligands involves conjugation of pre-existing chelating arms to a three dimensional framework (e.g. commercially available tren or a cheap industrial material 1,1,1-tris(hydroxymethyl)ethane). Cooper and co-workers<sup>34–36</sup> have successfully used this principle to build a tripodal hexadentate thioether ( $\text{S}_6$ ) ligand (1,1,1-tris[(2-methylthioethylthio)methyl]ethane).<sup>34</sup> Studies have shown that the tripodal  $\text{S}_6$  ligand coordinates to transition metals (e.g.  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ ) as well as does macrocyclic [18]ane $\text{S}_6$ .<sup>35,36</sup> The hexadentate amine ( $\text{N}_6$ ) analogues have also been described in the synthesis of sepulchrates.<sup>37,38</sup>

Recently, we reported several heptadentate  $\text{N}_4\text{O}_3$  amine phenols (**3**:  $\text{R} = \text{N}$ ,  $\text{X} = \text{NH}$ ,  $\text{Y} = \text{OH}$ ), which are the reduction products of Schiff bases derived from tren and salicylaldehyde or its ring-substituted derivatives.<sup>2,3</sup> These tribasic  $\text{N}_4\text{O}_3$  amine phenols readily form complexes with lanthanide and group 13 metal ions. In the present study, we have prepared a hexadentate  $\text{N}_3\text{O}_3$  amine phenol ligand system (**3**:  $\text{R} = \text{CH}_3\text{C}$ ,  $\text{X} = \text{NH}$ ,  $\text{Y} = \text{OH}$ ) using tame. Since the three chelating arms in  $\text{N}_3\text{O}_3$  amine phenol are bridged by a C atom, they are more preorganized than their  $\text{N}_4\text{O}_3$  analogues, in which the three chelating arms are bridged

by an N atom which can undergo a pyramidal inversion.<sup>39</sup> Extension of this general strategy will produce a variety of well preorganized polydentate tripodal ligands systems.

Previously, we found that the coordination behavior of  $\text{N}_4\text{O}_3$  amine phenols is largely dependent on the size of the coordinated metal ions.<sup>2,3</sup> The results reported here clearly show that changing the tertiary N-bridged framework to a C-bridged framework has a profound effect on the coordination behavior of these polydentate amine phenol ligands. The hexadentate  $\text{N}_3\text{O}_3$  amine phenol ligands are better tailored for six-coordination towards  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and  $\text{In}^{3+}$  to give neutral complexes  $[\text{M}(\text{N}_3\text{O}_3)]$ , even though the ionic radii of these metal ions are considerably varied.

The bond angles *A*, *B* and *C* (Chart I) can be used as a measure of whether the cavity of the coordinated amine phenol ligand matches the size of the metal ion. In the aluminum complex, [Al(IIc)], these bond angles suffer little deviation from tetrahedral values (within the experimental error). As the six coordinate ionic radii increase from 0.53 Å for  $\text{Al}^{3+}$ , to 0.62 Å for  $\text{Ga}^{3+}$  and 0.80 Å for  $\text{In}^{3+}$ ,<sup>40</sup> bond angles between the apical carbon atom and the methylene carbon atoms of the three chelating arms (angles *A*) are slightly compressed, while the angles *B* and *C* are slightly expanded. Apparently, the cavity in the tame-based  $\text{N}_3\text{O}_3$  amine phenol ligands matches the size of  $\text{Al}^{3+}$  best and the coordinated ligand framework suffers its greatest deformation in the indium complex [In(IIa)]· $\text{H}_2\text{O}$ . Stability constant studies (currently undergoing) will better quantify this fit.

The fact that the  $\text{N}_3\text{O}_3$  amine phenols reported in the present study form six-coordinated complexes with  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ , and  $\text{In}^{3+}$  ions suggests that the cavity of tame-based  $\text{N}_3\text{O}_3$  amine phenol ligand is quite flexible through the three chelating arms; this flexibility is evinced by the small changes in the *A*, *B* and *C* angles. (There are no significant changes in these angles within the experimental error from the Al complex to the Ga complex and from the Ga complex to the In complex; a slight but significant difference is observed between the Al and In complexes.) The relatively small deformation of the coordinated amine phenol ligand in [In(IIa)]· $\text{H}_2\text{O}$  suggests that coordination to a large metal ion (e.g.  $\text{In}^{3+}$ ) does not impart significant strain on the coordinated ligand framework. This augurs well for the coordination chemistry with tri- or tetravalent first-row (e.g.  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$ ) and second-row (e.g.  $\text{Tc}^{3+}$  and  $\text{Tc}^{4+}$ )

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transition metal ions. Indeed, these  $N_3O_3$  amine phenols form  $Fe^{3+}$  and  $Co^{3+}$  complexes, the properties of which will be reported later.

**Summary.** A new series of  $N_3O_3$  amine phenols has been readily prepared by  $KBH_4$  reduction of Schiff bases formed from the reactions of tame with salicylaldehyde or its ring-substituted derivatives. These tribasic  $N_3O_3$  amine phenols form six-coordinated neutral complexes  $[M(N_3O_3)]$  with  $Al^{3+}$ ,  $Ga^{3+}$  and  $In^{3+}$ . The determination of stability constants for aluminum, gallium and indium complexes of the tame-based  $N_3O_3$  amine phenol ligands will provide a better understanding of their solution behavior and of the biodistribution properties of their  $^{67}Ga$ - and  $^{111}In$ -labeled complexes. Further extension of this general synthetic strategy will produce a variety of polydentate tripodal ligands (e.g.  $N_3O_3$  (amine phenol),  $N_3O_3$ (amine carboxylate)

and  $N_3S_3$ (amine thiol)) by using various three-dimensional triamine frameworks. These studies are in progress.

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**Supplementary Material Available:** Complete tables of crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond distances and angles, torsion angles, intermolecular contacts, and least-squares planes for  $\{[Al(IIc)]_4[Na(H_2O)_2]\}(ClO_4)_2 \cdot 6.22H_2O$ ,  $[Ga(IIa)] \cdot 4.4H_2O$ , and  $[In(IIa)] \cdot 4.6H_2O$  (72 pages). Ordering information is given on any current masthead page.