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Gallium and Indium Complexes of Hexadentate Ligands Containing Pendant Pyridyl and Phenolate Groups

Ernest Wong,[1a] Shuang Liu,[1b] Steven J. Rettig,[1a] and Chris Orvig*,[1a]

Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia V6T 1Z1, Canada

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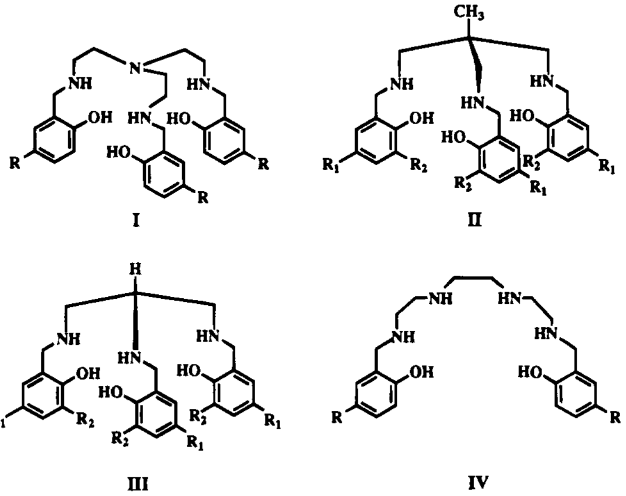
Gallium and indium complexes of *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)ethylenediamine (H_2**bbpen**), *N,N'*-bis(5-bromo-2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)ethylenediamine (H_2**Brbbpen**), and *N,N'*-bis(5-chloro-2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)ethylenediamine (H_2**Clbbpen**) were prepared and characterized by spectroscopic techniques and crystallographic analyses. H_2**bbpen**, H_2**Brbbpen**, and H_2**Clbbpen** were prepared in excellent yield by the reactions of 2-picolyl chloride with *N,N'*-bis(2-hydroxybenzyl)ethylenediamine (H_2bben), *N,N'*-bis(5-bromo-2-hydroxybenzyl)ethylenediamine (H_2Brbben), and *N,N'*-bis(5-chloro-2-hydroxybenzyl)ethylenediamine (H_2Clbben), respectively. Characterization of H_2**bbpen** and its substituted analogs showed these compounds to be symmetrical about the ethylene moiety of the ethylenediamine backbone. This symmetry is maintained in the metal complexes of these compounds. There are six potential sites for coordination to a metal ion: two amine nitrogens, two phenolate oxygens, and two pyridyl nitrogens. A series of monocationic metal complexes were obtained from the reactions of Ga^{3+} and In^{3+} with H_2**bbpen**, H_2**Brbbpen**, and H_2**Clbbpen** in the presence of 2 equiv of base (acetate). Crystals of [Ga(**Clbbpen**)]ClO_4 are triclinic, of space group $P\bar{1}$, with $a = 11.1563(6)$ Å, $b = 14.1365(6)$ Å, $c = 9.9296(7)$ Å, $\alpha = 98.395(4)°$, $\beta = 107.094(5)°$, $\gamma = 70.751(4)°$, and $Z = 2$, and those of [In(**Clbbpen**)]ClO_4 are monoclinic, of space group $P2_1/c$, with $a = 9.693(1)$ Å, $b = 21.821(2)$ Å, $c = 14.428(1)$ Å, $\beta = 109.413(7)°$, and $Z = 4$. The structures were solved by heavy atom methods and were refined by full-matrix least-squares procedures to $R = 0.035$ and 0.030 for 5777 and 6002 reflections with $I \geq 3\sigma(I)$, respectively. Both Ga^{3+} and In^{3+} were coordinated in a distorted octahedral geometry by an $N_2N'_2O_2$ donor set. Greater distortion was observed in the octahedral geometry of the [In(**Clbbpen**)]ClO_4 complex versus the [Ga(**Clbbpen**)]ClO_4 complex. ^1H NMR spectral data of the metal complexes showed rigid solution structures for all the Ga and In complexes; no evidence of fluxional behavior was observed at solution temperatures as high as 120 °C.

Introduction

The coordination chemistry of group 13 metal ions is of interest to us because of its role in the genesis and diagnosis of diseases. Recently, we reported group 13 metal complexes with several series of polydentate amine phenols which differed in amine backbone (Chart 1): tris(2-aminoethyl)amine (tren) based potentially N_4O_3 amine phenols **I**;[2] 1,1,1-tris(aminomethyl)ethane (tame) based potentially N_3O_3 amine phenols **II**;[3] 1,2,3-triaminopropane (tap) based potentially N_3O_3 amine phenols **III**;[4] and triethylenetetramine (trien) based potentially N_4O_2 amine phenols **IV**.[5] Tripodal and linear amine phenol complexes with lanthanide metal ions were also reported.[6−9] In previous studies of group 13 metal complexes with amine phenol ligands, the binding selectivity of the various amine phenols (Chart 1) for group 13 metal ions was examined by varying the spatial arrangements of the amine nitrogen and phenolate oxygen donor atoms.[2−5] However, binding selectivity of polydentate ligands can also be adjusted by the alteration or incorporation of different donor atoms. As an extension of our investigation into the coordination of Ga^{3+} and In^{3+} with polydentate ligands,

Chart 1



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* To whom correspondence should be addressed. Tel: 604-822-4449. Fax: 604-822-2847. Internet: ORVIG@CHEM.UBC.CA.

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(1) (a) University of British Columbia. (b) NSERC of Canada Postdoctoral Fellow, 1991−1993. Present address: Radiopharmaceutical Division, Dupont-Merck Pharmaceutical Co., 331 Treble Cove Rd., N. Billerica, MA 01862.

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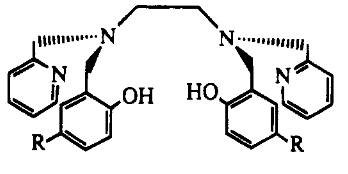
we have incorporated pyridyl nitrogen atoms into the amine phenol donor set.

Numerous investigations of Cu, Co, Fe, Mn, and Zn complexes with multinucleating ligands containing phenolate and/or pyridyl pendant groups have been reported.[10-18] For the most part, the objectives of these investigations were to determine the structure and physical properties and to reproduce the coordination of multimetallic sites of metalloproteins. Pyridyl and/or phenolate groups are incorporated into the multinucleating ligands used in these metalloprotein modeling studies because phenolate and pyridyl groups have the potential to mimic, respectively, the coordinating moieties of the amino acids tyrosine and histidine, which are present in the active sites of metalloproteins. Other pendant groups such as pyrazole, benzimidazole, and imidazole are also used as analogs of the histidine imidazole functionality. Besides the interest in metalloproteins, polypyridyl ligands have a potential application as heavy metal chelators in biochemical studies. *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)ethylenediamine (tpen) was used as a heavy-metal chelator in studies measuring free cytosolic Ca^{2+} in Ehrlich and Yoshida ascites carcinomas[19] and in studies on the effect of iron-chelating agents on the toxicity of doxorubicin to MCF-7 human breast cancer cells.[20] Methylpyridyl-substituted ethylenediamine compounds were also examined for antihistaminic and antispasmodic activities.[21]

In this paper, we present the coordination of Ga^{3+} and In^{3+} with a series of potentially $N_2N'_2O_2$ ligands (H_2**bbpen**, H_2**Brbbpen**, H_2**Clbbpen**) which possess amine nitrogen, pyridyl



H_2bbpen: R=H
H_2Clbbpen: R=Cl
H_2Brbbpen: R=Br

nitrogen, and phenolate oxygen donor atoms. Manganese and vanadium complexes with the unsubstituted $N_2N'_2O_2$ H_2**bbpen** ligand have been reported as models for manganese-[22] and vanadium-containing[23] metalloenzymes. Coordination of this series of potential $N_2N'_2O_2$ ligands (H_2**bbpen**, H_2**Brbbpen**, H_2**Clbbpen**) to Ga^{3+} and In^{3+} is expected to yield monocationic complexes, which have the potential to be of interest in nuclear medicine applications, in myocardial imaging in particular.

Experimental Section

Materials. Ethylenediamine, 2-picolyl chloride hydrochloride, salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, potassium borohydride, and hexadecyltrimethylammonium bromide were obtained from Aldrich Chemicals. Hydrated Ga and In salts were obtained from Alfa Chemicals. All chemicals were used as received.

Instrumentation. NMR spectra were recorded on Bruker AC-200E (^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{13}C APT NMR) and Varian XL 300 (^{1}H, VT NMR) spectrometers and are reported as δ in ppm from external TMS. Mass Spectra (Cs^+ LSIMS) were obtained on a Kratos Concept II H32Q instrument with 3-nitrobenzyl alcohol or thioglycerol as the matrix. Infrared spectra were recorded as KBr disks on a Perkin-Elmer PE 783 spectrophotometer in the range 4000–400 cm^{-1} and were referenced to polystyrene film (data are found in Table 1). Melting points were measured on a Mel-Temp apparatus and were uncorrected. C, H, N analyses were performed by Mr. Peter Borda of UBC. Conductance measurements were made with a Yellow Springs YS-1 Model 35 conductance meter with solute concentration of 10^{-3} M at 25 °C.

Schiff Bases. *N,N′*-Bis(salicylidene)ethylenediamine (H_2salen) was prepared according to the method of Diehl and Hach.[24] *N,N′*-Bis(5-chlorosalicylidene)ethylenediamine (H_2Clsalen) and *N,N′*-bis(5-bromosalicylidene)ethylenediamine (H_2Brsalen) were prepared in a similar manner using 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde, respectively. All Schiff base compounds were prepared in excellent yields (93–97%).

Amine Phenols. *N,N′*-Bis(2-hydroxybenzyl)ethylenediamine (H_2bben) was prepared according to reported method with some modification.[25] KBH_4 (5.4 g, 0.1 mol) was added in small portions to a hot suspension of H_2salen (26.8 g, 0.1 mol) in methanol (50 mL). The yellow H_2salen dissolved in methanol as KBH_4 was slowly added to the suspension. After the addition of KBH_4, the solution was stirred and gently heated for 1 h. A white precipitate formed as the solution cooled to room temperature, and additional precipitate was obtained when an aqueous ammonium acetate solution (15 g, 0.2 mol in 50 mL) was added to the methanol solution at room temperature. The precipitate was collected by vacuum filtration and washed with cold methanol and diethyl ether. The white powder was then dried under vacuum at 60 °C for 24 h. Yield: 23 g (85%). Anal. Calcd (found) for $C_{16}H_{20}N_2O_2$: C, 70.56 (70.56); H, 7.40 (7.53); N, 10.29 (10.49).

N,N′-Bis(5-chloro-2-hydroxybenzyl)ethylenediamine (H_2Clbben) was prepared in the same manner using H_2Clsalen (33.7 g, 0.1 mol). Yield: 29 g (85%). Anal. Calcd (found) for $C_{16}H_{18}Cl_2N_2O_2$: C, 56.32 (56.17); H, 5.32 (5.47); N, 8.21 (8.09). *N,N′*-Bis(5-bromo-2-hydroxybenzyl)ethylenediamine (H_2Brbben) was prepared in the same manner using H_2Brsalen (42.6, 0.1 mol). Yield: 30 g (70%). Anal. Calcd (found) for $C_{16}H_{18}Br_2N_2O_2$: C, 44.68 (44.79); H, 4.22 (4.32); N, 6.51 (6.45).

Pyridyl Amine Phenols. *N,N′*-Bis(2-hydroxybenzyl)-*N,N′*-bis(2-methylpyridyl)ethylenediamine (H_2**bbpen**) was prepared in excellent yield according to the reported method with some modifications.[22] A solution of 2-(chloromethyl)pyridine hydrochloride (10 g, 60 mmol) in 50 mL of water was neutralized with 4 M NaOH to a pH between 10 and 11. H_2bben (8.15 g, 30 mmol) was then added to the solution. Both 2-(chloromethyl)pyridine and H_2bben were insoluble in basic aqueous solution so hexadecyltrimethylammonium bromide (0.36 g, 1 mmol) was added as a phase transfer catalyst. The mixture was stirred at room temperature and pH 10–11 for 24 h, during which time a white precipitate formed. The white precipitate was collected by vacuum filtration and washed with water and diethyl ether. It was then dried in vacuo at 60 °C. Yield: 13.2 g (90%). Mp: 116 °C. Anal. Calcd (found) for $C_{28}H_{30}N_4O_2$: C, 73.98 (74.16); H, 6.65 (6.90); N, 12.33 (11.86). Mass spectrum (LSIMS): m/z = 455 ($[M + 1]^+$, $[C_{28}H_{31}N_4O_2]^+$). Infrared spectral data are listed in Table 1. Tables

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Table 1. IR Spectral Data (cm^{-1}, KBr disk) for H$_2$**bbpen**, H$_2$**Brbbpen**, and H$_2$**Clbbpen** and Their Ga and In Complexes

compound	ν_{OH}	ν_{CH}	$\nu_{C=N}$, $\nu_{C=C}$
H$_2$**bbpen**	3600–3400 b, w	3100–2800 m	1615 s; 1598 s; 1590 s; 1575 s; 1500–1440 s
H$_2$**Clbbpen**	3600–3400 b, w	3100–2800 m	1615 s; 1598 s; 1590 s; 1575 s; 1500–1440 s
H$_2$**Brbbpen**	3600–3400 b, w	3100–2800 m	1615 s; 1598 s; 1590 s; 1575 s; 1500–1440 s
[Ga(**bbpen**)]ClO$_4$	3640–3340 b, m	3070–2900 m	1610 s; 1600 s; 1575 m; 1565 m; 1500–1400 s
[Ga(**Clbbpen**)]ClO$_4$	3640–3440 b, m	3100–2850 m	1615 s; 1605 s; 1575 m; 1560 m; 1500–1410 s
[Ga(**Brbbpen**)]ClO$_4$	3640–3340 b, m	3120–2800 m	1610 s; 1580 m; 1570 m; 1550 s; 1500–1410 s
[In(**bbpen**)]ClO$_4$	3660–3300 b, s	3080–2800 m	1610 s; 1595 s; 1575 m; 1565 m; 1500–1410 s
[In(**Clbbpen**)]ClO$_4$	3640–3340 b, m	3100–2800 m	1615 s; 1575 m; 1570 m; 1500–1410 s
[In(**Brbbpen**)]Cl	3660–3300 b, m	3100–2800 m	1615 s; 1575 m; 1570 m; 1500–1410 s

Table 2. Analytical [Calcd (Found)], LSIMS Mass Spectral[a], and Conductance (Ω^{-1} mol^{-1} cm^2) Data for the Ga and In Complexes of H$_2$**bbpen**, H$_2$**Brbbpen**, and H$_2$**Clbbpen**

complex	C	H	N	*m/z*	molar conductance
[Ga(**bbpen**)]ClO$_4$·2.5H$_2$O	50.44 (50.20)	4.99 (4.67)	8.40 (8.33)	521 [ML]$^+$, 1143 [2(ML)(A)]$^+$	119
[Ga(**Clbbpen**)]ClO$_4$	48.70 (48.74)	3.79 (3.87)	8.11 (8.15)	591 [ML]$^+$, 1281 [2(ML)(A)]$^+$	121
[Ga(**Brbbpen**)]ClO$_4$	43.14 (43.18)	3.36 (3.36)	7.19 (7.09)	679 [ML]$^+$, 1459 [2(ML)(A)]$^+$	122
[In(**bbpen**)]NO$_3$	53.43 (53.38)	4.48 (4.59)	11.13 (11.04)	567 [ML]$^+$, 1196 [2(ML)(A)]$^+$	119
[In(**bbpen**)]ClO$_4$·H$_2$O	49.11 (49.32)	4.42 (4.35)	8.18 (7.89)	567 [ML]$^+$	119
[In(**Clbbpen**)]ClO$_4$·H$_2$O	44.62 (44.96)	3.74 (3.80)	7.43 (7.40)	635 [ML]$^+$	122
[In(**Brbbpen**)]Cl·0.5H$_2$O	40.34 (40.35)	3.26 (3.37)	6.72 (6.63)	725 [ML]$^+$	123

[a] ML indicates metal ion-containing cation; A indicates anion.

of ^{1}H and ^{13}C NMR spectral data are available as part of the supplementary material.

N,N'-Bis(5-chloro-2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)ethylenediamine (H$_2$**Clbbpen**) was prepared in a similar manner using H$_2$Clbben. The reaction mixture of 2-(chloromethyl)pyridine hydrochloride (10 g, 60 mmol), *N,N'*-bis(5-chloro-2-hydroxybenzyl)ethylenediamine (10.2 g, 30 mmol), and hexadecyltrimethylammonium bromide (0.36 g, 1 mmol) in 50 mL of water was stirred for 48 h at room temperature and pH 10–11. The white precipitate formed during the 48 h period. Yield: 14.3 g (91%). Mp: 115 °C. Anal. Calcd (found) for C$_{28}$H$_{28}$Cl$_2$N$_4$O$_2$: C, 64.25 (64.23); H, 5.39 (5.19); N, 10.70 (10.43). Mass spectrum (LSIMS): m/z = 523 ([M + 1]$^+$, [C$_{28}$H$_{29}$Cl$_2$N$_4$O$_2$]$^+$). Infrared spectral data are listed in Table 1. Tables of ^{1}H and ^{13}C NMR spectral data are available as part of the supplementary material.

N,N'-Bis(5-bromo-2-hydroxybenzyl)-*N,N'*-bis(2-methylpyridyl)ethylenediamine (H$_2$**Brbbpen**) was prepared in a similar manner using H$_2$Brbben. The reaction mixture of 2-(chloromethyl)pyridine hydrochloride (10 g, 60 mmol), *N,N'*-bis(5-bromo-2-hydroxybenzyl)ethylenediamine (12.9 g, 30 mmol), and hexadecyltrimethylammonium bromide (0.36 g, 1 mmol) in 50 mL of water was stirred for 48 h at room temperature and pH 10–11. The white precipitate formed during the 48 h period. Yield: 17.0 g (93%). Mp: 115 °C. Anal. Calcd (found) for C$_{28}$H$_{28}$Br$_2$N$_4$O$_2$: C, 54.92 (55.23); H, 4.61 (4.67); N, 9.15 (9.26). Mass spectrum (LSIMS): m/z = 613 ([M + 1]$^+$, [C$_{28}$H$_{29}$Br$_2$N$_4$O$_2$]$^+$). Infrared spectral data are listed in Table 1. Tables of ^{1}H and ^{13}C NMR spectral data are available as part of the supplementary material.

Synthesis of Metal Complexes. As many of the syntheses were similar to each other, detailed procedures are only given for representative examples. All Ga and In complexes which were prepared, along with their analytical and mass spectral data, are listed in Table 2, while infrared spectral data are given in Table 1. Molar conductance measurements of the metal complexes (10^{-3} M in acetonitrile, 25 °C) are also given in Table 2. ^{1}H and ^{13}C NMR spectra of all metal complexes were obtained in DMSO-d_6. ^{1}H NMR spectral data are listed in Table 3. The synthesis of Ga and In complexes described below employed the perchlorate salts of the respective metal ions, but other Ga or In salts can also be used.

N.B. It should be noted that perchlorate salts of metal complexes are potentially explosive and should be handled with care.

[Ga(Clbbpen)][ClO$_4$]·H$_2$O. To a solution of Ga(ClO$_4$)$_3$·6H$_2$O (300 mg, 0.630 mmol) and H$_2$**Clbbpen** (400 mg, 0.764 mmol) in methanol (15 mL) was added NaOAc (126 mg, 1.54 mmol) in methanol (5 mL). The mixture was immediately filtered, and the filtrate was left to stand at room temperature. Slow evaporation of the solvent yielded a beige crystalline precipitate, which was collected by filtration, washed with cold methanol, followed by diethyl ether, and then dried in vacuo at 80 °C to yield 275 mg (74%). Recrystallization of this precipitate from methanol afforded crystals suitable for elemental and X-ray crystallographic analysis.

[In(Clbbpen)][ClO$_4$]. To a solution of In(ClO$_4$)$_3$·8H$_2$O (300 mg, 0.538 mmol) and H$_2$**Clbbpen** (350 mg, 0.669 mmol) in methanol (15 mL) was added NaOAc (110 mg, 1.34 mmol) in methanol (5 mL). The same workup as for the Ga analog yielded 263 mg (77%). Recrystallization from methanol afforded crystals suitable for elemental and X-ray crystallographic analysis.

X-ray Crystallographic Analyses of [M(Clbbpen)]ClO$_4$ (M = Ga, In). Selected crystallographic data appear in Table 4. The final unit-cell parameters were obtained by least-squares calculations on the setting angles for 25 reflections with 2θ = 40.7–43.2° for [Ga(**Clbbpen**)]ClO$_4$ and 37.6–43.3° for [In(**Clbbpen**)]ClO$_4$. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for both complexes. The data were processed[26] and corrected for Lorentz and polarization effects and for absorption (empirical, based on azimuthal scans for three reflections).

Both structures were solved by conventional heavy atom methods. The structure analysis of the gallium complex was initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the E statistics and the Patterson function. This choice was confirmed by subsequent calculations. The perchlorate group is disordered with respect to a rotation about the Cl3–O3 bond in the indium structure. A 2-fold split atom model was employed for the other three oxygen atoms. A constrained group occupancy factor was refined.

All non-hydrogen atoms of both structures were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Secondary extinction corrections were not necessary. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 27. Final atomic coordinates and equivalent isotropic thermal parameters and selected bond lengths and bond angles appear in Tables 5 and 6 for [Ga(**Clbbpen**)]ClO$_4$ and in Tables 7 and 8 for [In(**Clbbpen**)]ClO$_4$. Complete tables of crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, and bond angles for both structures are included as supplementary material.

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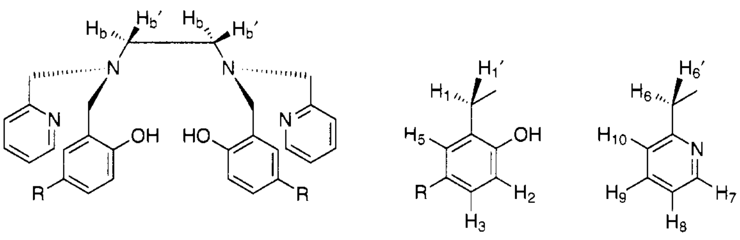
Table 3. ^{1}H NMR Data (300 MHz, DMSO-d_6) for Ga and In Complexes of H_2**bbpen**, H_2**Brbbpen**, and H_2**Clbbpen**



(R = H_4 for H_2 **bbpen**)

assignt	[Ga(**bbpen**)]ClO$_4$	[Ga(**Clbbpen**)]ClO$_4$	[Ga(**Brbbpen**)]ClO$_4$	[In(**bbpen**)]ClO$_4$	[In(**Clbbpen**)]ClO$_4$	[In(**Brbbpen**)]ClO$_4$
H_b	2.93 (d, 2H)	2.93 (d, 2H)	2.95 (d, 2H)	3.18 (d, 2H)	3.12 (d, 2H)	3.12 (d, 2H)
H_b'	3.28 (d, 2H)	3.30 (d, 2H)	3.29 (d, 2H)	3.25 (d, 2H)	3.26 (d, 2H)	3.26 (d, 2H)
H_1	3.85 (d, 2H)	3.82 (d, 2H)	3.80 (d, 2H)	3.85 (d, 2H)	3.84 (d, 2H)	3.84 (d, 2H)
H_1'	3.95 (d, 2H)	4.02 (d, 2H)	4.00 (d, 2H)	4.10 (d, 2H)	3.92 (d, 2H)	3.92 (d, 2H)
H_2	6.48 (d, 2H)	6.50 (d, 2H)	6.46 (d, 2H)	6.22 (d, 2H)	6.16 (d, 2H)	6.16 (d, 2H)
H_3	6.57 (td, 2H)	7.00 (dd, 2H)	7.12 (dd, 2H)	6.45 (dd, 2H)	6.87 (dd, 2H)	6.87 (dd, 2H)
H_4	7.00 (m, 2H)			6.85 (td, 2H)		
H_5	7.00 (m, 2H)	7.10 (d, 2H)	7.20 (d, 2H)	7.05 (dd, 2H)	7.12 (d, 2H)	7.12 (d, 2H)
H_6	4.34 (d, 2H)	4.37 (d, 2H)	4.42 (d, 2H)	4.17 (d, 2H)	4.13 (d, 2H)	4.13 (d, 2H)
H_6'	4.48 (d, 2H)	4.52 (d, 2H)	4.52 (d, 2H)	4.32 (d, 2H)	4.26 (d, 2H)	4.26 (d, 2H)
H_7	8.69 (d, 2H)	8.65 (d, 2H)	8.64 (d, 2H)	8.80 (d, 2H)	8.80 (d, 2H)	8.80 (d, 2H)
H_8	8.10 (td, 2H)	8.13 (td, 2H)	8.18 (td, 2H)	8.00 (td, 2H)	8.06 (td, 2H)	8.06 (td, 2H)
H_9	7.62 (td, 2H)	7.67 (td, 2H)	7.69 (td, 2H)	7.60 (td, 2H)	7.60 (td, 2H)	7.60 (td, 2H)
H_{10}	7.48 (d, 2H)	7.58 (d, 2H)	7.57 (d, 2H)	7.25 (d, 2H)	7.40 (d, 2H)	7.40 (d, 2H)

Table 4. Selected Crystallographic Data for [Ga(**Clbbpen**)]ClO$_4$ and [In(**Clbbpen**)]ClO$_4$

compound	[Ga(**Clbbpen**)]ClO$_4$	[In(**Clbbpen**)]ClO$_4$
formula	$C_{28}H_{26}Cl_3GaN_4O_6$	$C_{28}H_{26}Cl_3InN_4O_6$
fw	690.62	735.72
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.1563(6)	9.693(1)
b, Å	14.1365(6)	21.821(2)
c, Å	9.9296(7)	14.428(1)
α, deg	98.395(4)	90
β, deg	107.094(5)	109.413(7)
γ, deg	70.751(4)	90
V, Å^3	1411.1(2)	2878.2(5)
Z	2	4
ϱ_{calc}, g/cm^3	1.625	1.698
T, °C	21	21
radiation	Mo Kα	Mo Kα
λ, Å	0.710 69	0.710 69
μ, cm^{-1}	13.10	11.37
transm factors	0.82–1.00	0.84–1.00
$R(F)^a$	0.035	0.030
$R_w(F)^b$	0.031	0.029

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Results and Discussion

Ligand Syntheses. Pyridyl amine phenols (H_2**bbpen**, H_2**Clbbpen**, H_2**Brbbpen**) were prepared in good yield according to the reported method with some improvements (Scheme 1).[22,23] The three steps in the preparation of each pyridyl amine phenol involved the condensation reaction of ethylenediamine and the appropriate salicylaldehyde to produce the Schiff base, followed by the reduction of the Schiff base with potassium borohydride to produce the corresponding amine phenol and reaction of the amine phenol with 2-(chloromethyl)pyridine at pH 10−11 in the presence of hexadecyltrimethylammonium bromide (which acts as a phase transfer catalyst). These ethylenediamine based compounds were soluble in polar solvents such as methanol, chloroform, and acetone, and were hydrolytically stable under both acidic and basic conditions. They were also water soluble at low pH in millimolar concentration.

NMR spectral data of H_2**bbpen**, H_2**Clbbpen**, and H_2**Brbbpen** indicated them to be symmetrical about the ethylene moiety of the ethylenediamine backbone. The ^{1}H NMR spectrum of H_2**Clbbpen** in $CDCl_3$ is shown in Figure 1 (top). The two hydroxybenzyl groups were spectroscopically equivalent, as were the two pyridylmethyl moieties. A single set of ^{1}H resonance signals in the region 6.5−7.15 ppm was observed for the hydrogen atoms on the two equivalent hydroxybenzyl groups. The set of resonance signals in the 7.15−8.6 ppm region was attributed to the eight hydrogen atoms on the two equivalent methylpyridyl groups. The singlet at 3.65 ppm corresponded to the four benzylic hydrogens, while the singlet at 3.74 ppm corresponded to the four methylene hydrogens on the two equivalent methylpyridyl arms. The four ethylene hydrogens on the ethylenediamine backbone appeared as a singlet at 2.70 ppm. Only 14 out of a possible 28 ^{13}C resonance signals were observed in the ^{13}C NMR spectra. Elemental analyses and infrared and mass spectral data were consistent with the NMR spectral data.

Ga and In Complexes. Monocationic Ga and In complexes were easily prepared from reactions of H_2**bbpen**, H_2**Brbbpen**, and H_2**Clbbpen** with hydrated metal salts in the presence of excess sodium acetate. The complexes were found to be stable under both basic (no metal hydroxide formed in the presence of sodium hydroxide) and weakly acidic conditions (stable to acetic acid formed upon the coordination of the metal ion by the ligand in the presence of sodium acetate). The Ga and In complexes were soluble in dimethyl sulfoxide and slightly soluble in alcohols and in weakly acidic solution (pH ~ 2). The metal complexes were characterized by spectroscopic techniques (IR, NMR, and LSIMS), conductivity measurements, and elemental analyses (Tables 1−3). All data were consistent with the proposed formulation of monocationic, hexacoordinated complexes in which the metal ion is coordinated to two amine nitrogen atoms, two pyridyl nitrogen atoms, and two phenolate oxygen atoms (an $N_2N'_2O_2$ donor atom set). X-ray crystallographic analyses of [Ga(**Clbbpen**)]ClO$_4$ and [In(**Clbbpen**)]ClO$_4$ were performed and found to be consistent with the proposed formulation (*vide infra*).

Attempts to isolate analytically pure Al^{3+} complexes were unsuccessful, even in the presence of excess ligand, as precipitation of aluminum hydroxide often interfered with, and ac-

Table 5. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2) for Non-Hydrogen Atoms in [Ga(**Clbbpen**)]ClO$_4$

atom	*x*	*y*	*z*	$B_{eq}{}^a$
Ga1	0.37827(3)	0.19882(2)	0.39109(3)	2.146(5)
Cl1	0.93307(7)	−0.04954(6)	0.09009(8)	4.56(2)
Cl2	−0.17793(6)	0.32092(6)	0.69529(7)	3.98(2)
Cl3	0.76501(7)	0.39886(5)	0.18380(7)	3.66(2)
O1	0.4687(2)	0.0787(1)	0.3122(2)	2.82(4)
O2	0.2487(1)	0.1507(1)	0.4123(2)	2.64(4)
O3	0.8574(2)	0.4535(1)	0.2305(2)	5.20(6)
O4	0.6843(4)	0.4335(2)	0.0550(3)	12.3(1)
O5	0.8244(3)	0.2952(2)	0.1672(3)	8.19(8)
O6	0.6897(3)	0.4157(2)	0.2810(3)	9.44(10)
N1	0.5007(2)	0.2759(1)	0.3451(2)	2.37(4)
N2	0.3062(2)	0.3399(1)	0.5020(2)	2.26(4)
N3	0.2582(2)	0.2616(1)	0.1968(2)	2.53(4)
N4	0.5071(2)	0.1708(1)	0.5941(2)	2.38(4)
C1	0.4874(2)	0.3693(2)	0.4379(3)	3.01(5)
C2	0.3475(2)	0.4144(2)	0.4490(3)	2.88(5)
C3	0.6413(2)	0.2112(2)	0.3764(2)	2.61(5)
C4	0.6604(2)	0.1134(2)	0.2888(2)	2.40(5)
C5	0.5746(2)	0.0548(2)	0.2631(2)	2.41(5)
C6	0.6017(2)	−0.0353(2)	0.1810(3)	2.92(5)
C7	0.7108(3)	−0.0677(2)	0.1284(3)	3.32(6)
C8	0.7947(2)	−0.0096(2)	0.1558(3)	2.98(5)
C9	0.7696(2)	0.0802(2)	0.2339(3)	2.81(5)
C10	0.4531(2)	0.2998(2)	0.1937(3)	3.07(6)
C11	0.3096(2)	0.3105(2)	0.1342(2)	2.82(5)
C12	0.2351(3)	0.3663(2)	0.0181(3)	3.76(6)
C13	0.1052(3)	0.3686(2)	−0.0363(3)	4.36(7)
C14	0.0534(3)	0.3147(2)	0.0249(3)	4.04(7)
C15	0.1329(2)	0.2626(2)	0.1420(3)	3.22(6)
C16	0.1594(2)	0.3715(2)	0.4716(2)	2.45(5)
C17	0.1080(2)	0.2972(2)	0.5123(2)	2.32(5)
C18	0.1532(2)	0.1931(2)	0.4789(2)	2.35(5)
C19	0.0919(2)	0.1312(2)	0.5133(3)	2.98(5)
C20	−0.0092(2)	0.1692(2)	0.5779(3)	3.17(6)
C21	−0.0504(2)	0.2706(2)	0.6115(2)	2.91(5)
C22	0.0074(2)	0.3336(2)	0.5793(2)	2.76(5)
C23	0.3650(2)	0.3311(2)	0.6571(2)	2.93(5)
C24	0.4897(2)	0.2466(2)	0.6934(2)	2.50(5)
C25	0.5804(2)	0.2438(2)	0.8232(3)	3.22(6)
C26	0.6893(3)	0.1590(2)	0.8543(3)	3.64(6)
C27	0.7030(2)	0.0800(2)	0.5748(3)	3.44(6)
C28	0.6112(2)	0.0886(2)	0.6259(3)	2.72(5)

^{a} $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

companied, the isolation of the complexes. ^{1}H NMR spectra of freshly prepared solutions of Al(ClO$_4$)$_3$ and H$_2$**bbpen** showed the presence of the Al complex; however, precipitation of aluminum hydroxide from the solution occurred after 1 h at room temperature. Subsequent ^{1}H NMR spectra of the solution showed diminished intensities for the ^{1}H resonance signals attributed to the Al complex. This clearly indicated the instability of the Al complexes in solution and also indicated that the Al complexes were much less stable than their Ga congeners.

Infrared spectral data for H$_2$**bbpen**, H$_2$**Brbbpen**, and H$_2$**Clbbpen** showed strong to medium bands in the 1590−1575 cm^{-1} region corresponding to C=N stretching modes of the pyridyl groups. Upon coordination to Ga^{3+} or In^{3+}, there was a general bathochromic shift of ~15 cm^{-1} and a decrease in the intensity of the C=N stretching modes. Broad O−H stretching bands in the region 3600−3400 cm^{-1} suggested, in most cases, the presence of hydrogen bonding between the metal complexes and water molecules. Additional bands that were probably due to M−O and M−N stretches were observed; however, assignments of these bands were not conclusive because of their low energies. The infrared spectra of the metal complexes also exhibited strong broad perchlorate bands at ~1100 cm^{-1}.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for the [Ga(**Clbbpen**)]$^+$ Cation in [Ga(**Clbbpen**)]ClO$_4$

Ga−O1	1.860(2)	N2−C16	1.496(3)
Ga−O2	1.871(2)	N2−C23	1.492(3)
Ga−N1	2.180(2)	N3−C11	1.338(3)
Ga−N2	2.158(2)	N4−C24	1.351(3)
Ga−N3	2.121(2)	C1−C2	1.510(3)
Ga−N4	2.107(2)	C3−C4	1.510(3)
O1−C5	1.332(3)	C4−C5	1.409(3)
O2−C18	1.337(3)	C10−C11	1.499(3)
N1−C1	1.487(3)	C16−C17	1.501(3)
N1−C3	1.498(3)	C17−C18	1.412(3)
N1−C10	1.489(3)	C23−C24	1.493(3)
N2−C2	1.491(3)		
O1−Ga−O2	95.17(6)	Ga−N1−C1	106.3(1)
O1−Ga−N1	90.77(7)	Ga−N1−C3	110.3(1)
O1−Ga−N2	170.22(7)	Ga−N1−C10	109.5(1)
O1−Ga−N3	96.03(7)	Ga−N2−C2	105.9(1)
O1−Ga−N4	92.98(7)	Ga−N2−C16	110.9(1)
O2−Ga−N1	169.67(7)	Ga−N2−C23	110.1(1)
O2−Ga−N2	92.30(6)	Ga−N2−C10	110.0(6)
O2−Ga−N3	92.14(7)	Ga−N3−C11	116.4(2)
O2−Ga−N4	97.92(7)	Ga−N3−C15	124.0(2)
N1−Ga−N2	82.81(7)	Ga−N4−C24	116.2(1)
N1−Ga−N3	78.82(7)	Ga−N4−C28	125.5(2)
N1−Ga−N4	90.18(7)	C1−N1−C3	110.3(2)
N2−Ga−N3	89.97(7)	C1−N1−C10	110.8(2)
N2−Ga−N4	79.72(7)	C3−N1−C10	109.6(2)
N3−Ga−N4	165.83(7)	C2−N2−C23	110.6(2)
Ga−O1−C5	131.2(1)	C2−N2−C16	109.9(2)
Ga−O2−C18	130.1(1)	C16−N2−C23	109.3(2)

Molar conductivity measurements in acetonitrile of the Ga and In complexes showed values (Table 2) of 119−122 Ω^{-1} mol^{-1} cm^{-1} (25 °C); this was consistent with a 1:1 electrolyte,[28] *i.e.* a monocationic metal complex formulation. In the LSIMS of the Ga and In complexes, the molecular ion [ML]$^+$ peaks were detected as well as the dinuclear [(ML)$_2$A]$^+$ peaks, where A was the anion present in the complexes (Table 2). The dinuclear ion peaks, [(ML)$_2$A]$^+$, were probably caused by dimerization in the mass spectrometer. Dinuclear ion peaks, [M$_2$L$_5$]$^+$, have been previously observed in the mass spectra of tris(ligand) group 13 metal complexes.[29]

^{1}H NMR spectra of the metal complexes were recorded in DMSO-d_6 and were very similar to each other with the exception of the aromatic region (6.5−7.5 ppm). ^{1}H NMR spectra of [Ga(**Clbbpen**)]ClO$_4$ and [In(**Clbbpen**)]ClO$_4$ in DMSO-d_6 are given in Figure 1. The equivalence of the pendant arms was maintained in the Ga and In complexes of H$_2$**bbpen** and its substituted analogs. In the ^{1}H NMR spectra of the metal complexes, two sets of resonance signals were observed for the pyridyl groups (7.17−8.56 ppm) and for the hydroxybenzyl groups (6.75−7.15 ppm), and the ^{13}C NMR spectra of the complexes also showed the symmetrical nature of the metal complexes; only 14 of a possible 28 ^{13}C resonance signals were observed.

Upon coordination, the singlet at 3.6 ppm due to the four benzylic hydrogens H$_1$ became two doublets at ~3.8 and ~4.0 ppm. Since the ^{1}H NMR spectra of the metal complexes still showed the two hydroxybenzyl groups as chemically equivalent, the two doublets at ~3.8 and ~4.0 ppm must correspond to two nonequivalent hydrogens atoms on the same benzylic carbon. The methene hydrogens of the methylpyridyl groups also became nonequivalent upon complexation and appeared as a pair of doublets at ~4.3 and ~4.4 ppm. The two doublets at ~3.0 and ~3.25 ppm correspond to the two nonequivalent

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Table 7. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2) for Non-Hydrogen Atoms in [In(**Clbbpen**)]ClO$_4$

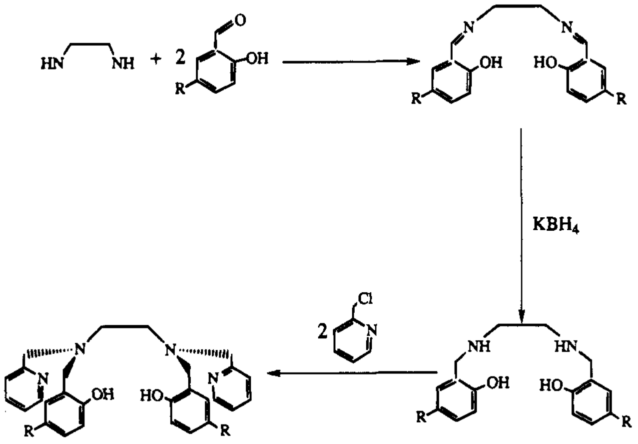
atom	*x*	*y*	*z*	B_{eq}[a]	occ
In1	0.37940(2)	0.533967(9)	0.31498(1)	2.750(3)	
Cl1	−0.02215(9)	0.75982(4)	0.48934(6)	4.72(2)	
Cl2	0.87957(9)	0.36259(4)	0.12489(7)	5.72(2)	
Cl3	−0.31020(8)	0.64470(4)	0.08925(6)	4.14(2)	
O1	0.3695(2)	0.56363(9)	0.4485(1)	3.31(4)	
O2	0.5981(2)	0.52306(9)	0.3354(1)	3.49(4)	
O3	−0.2285(3)	0.6742(1)	0.1782(2)	6.83(7)	
O4	−0.292(1)	0.6764(4)	0.0125(5)	8.8(2)	0.70(2)
O4a	−0.358(4)	0.684(1)	0.012(2)	16.8(7)	0.30
O5	−0.4622(7)	0.6453(4)	0.0790(7)	8.1(2)	0.70
O5a	−0.422(3)	0.617(2)	0.098(2)	16.2(10)	0.30
O6	−0.2700(9)	0.5832(2)	0.0880(7)	9.0(2)	0.70
O6a	−0.205(2)	0.609(1)	0.056(1)	11.5(6)	0.30
N1	0.1388(2)	0.5646(1)	0.2394(1)	3.06(5)	
N2	0.3222(2)	0.4811(1)	0.1686(1)	3.11(5)	
N3	0.3909(2)	0.6340(1)	0.2696(2)	3.36(5)	
N4	0.3113(2)	0.4391(1)	0.3478(1)	2.95(5)	
C1	0.0760(3)	0.5177(1)	0.1626(2)	3.82(6)	
C2	0.1805(3)	0.5064(2)	0.1049(2)	4.28(7)	
C3	0.0673(3)	0.5617(1)	0.3175(2)	3.23(6)	
C4	0.1293(3)	0.6100(1)	0.3947(2)	3.01(6)	
C5	0.2786(3)	0.6091(1)	0.4537(2)	3.08(6)	
C6	0.3322(3)	0.6573(1)	0.5193(2)	3.71(6)	
C7	0.2419(3)	0.7039(1)	0.5295(2)	4.10(7)	
C8	0.0956(3)	0.7027(1)	0.4735(2)	3.68(7)	
C9	0.0390(3)	0.6570(1)	0.4063(2)	3.39(6)	
C10	0.1286(3)	0.6277(1)	0.1983(2)	3.70(6)	
C11	0.2644(3)	0.6648(1)	0.2467(2)	3.42(6)	
C12	0.2607(4)	0.7265(1)	0.2634(2)	4.57(8)	
C13	0.3894(4)	0.7577(2)	0.3042(3)	5.52(9)	
C14	0.5197(4)	0.7266(2)	0.3249(3)	5.31(9)	
C15	0.5176(3)	0.6649(1)	0.3066(2)	4.12(7)	
C16	0.4412(3)	0.4968(1)	0.1271(2)	3.36(6)	
C17	0.5871(3)	0.4701(1)	0.1858(2)	3.02(5)	
C18	0.6555(3)	0.4844(1)	0.2861(2)	3.10(6)	
C19	0.7895(3)	0.4569(1)	0.3359(2)	3.78(7)	
C20	0.8579(3)	0.4191(1)	0.2874(2)	4.17(7)	
C21	0.7921(3)	0.4078(1)	0.1893(2)	4.01(7)	
C22	0.6571(3)	0.4320(1)	0.1386(2)	3.49(6)	
C23	0.3130(3)	0.4138(1)	0.1833(2)	3.81(7)	
C24	0.2881(3)	0.3967(1)	0.2775(2)	3.09(6)	
C25	0.2457(3)	0.3377(1)	0.2908(2)	4.10(7)	
C26	0.2244(4)	0.3227(1)	0.3778(3)	4.92(8)	
C27	0.2471(3)	0.3671(1)	0.4495(2)	4.34(8)	
C28	0.2907(3)	0.4248(1)	0.4332(2)	3.41(6)	

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for the [In(**Clbbpen**)]$^+$ Cation in [In(**Clbbpen**)]ClO$_4$

In−O1	2.064(2)	N2−C16	1.506(3)
In−O2	2.055(2)	N2−C23	1.491(4)
In−N1	2.320(2)	N3−C11	1.341(3)
In−N2	2.306(2)	N4−C24	1.334(3)
In−N3	2.291(2)	C1−C2	1.530(4)
In−N4	2.271(2)	C3−C4	1.505(4)
O1−C5	1.346(3)	C4−C5	1.414(4)
O2−C18	1.339(3)	C10−C11	1.505(4)
N1−C1	1.481(3)	C16−C17	1.503(4)
N1−C3	1.508(3)	C17−C18	1.412(3)
N1−C10	1.491(4)	C23−C24	1.504(4)
N2−C2	1.481(3)		
O1−In−O2	105.54(7)	In−N1−C1	104.6(2)
O1−In−N1	89.83(7)	In−N1−C3	106.1(1)
O1−In−N2	160.00(8)	In−N1−C10	112.1(2)
O1−In−N3	89.42(8)	In−N2−C2	105.9(2)
O1−In−N4	89.12(7)	In−N2−C16	105.5(1)
O2−In−N1	158.25(7)	In−N2−C23	111.7(1)
O2−In−N2	89.78(7)	In−N3−C11	114.9(2)
O2−In−N3	90.30(8)	In−N3−C15	119.3(2)
O2−In−N4	102.83(7)	In−N4−C24	117.4(2)
N1−In−N2	79.36(7)	In−N4−C28	122.9(2)
N1−In−N3	74.26(8)	C1−N1−C3	110.8(2)
N1−In−N4	92.50(8)	C1−N1−C10	112.5(2)
N2−In−N3	103.54(8)	C3−N1−C10	110.5(2)
N2−In−N4	74.73(7)	C2−N2−C23	111.5(2)
N3−In−N4	166.69(7)	C2−N2−C16	110.1(2)
In−O1−C5	121.2(1)	C16−N2−C23	111.7(2)
In−O2−C18	126.0(2)		

Scheme 1



hydrogen atoms on each methylene carbon of the ethylenediamine backbone.

As the NMR spectra of the Ga and In complexes were very similar, variable-temperature ^{1}H NMR experiments were only performed for [Ga(**bbpen**)]ClO$_4$ and [In(**bbpen**)]NO$_3$. No significant changes were observed in the ^{1}H NMR spectra of these metal complexes as the temperature was raised from room temperature to 120 °C. This clearly demonstrated the intact and rigid structure of the complexes in solution, minor shifts of the ^{1}H resonance signals, and a slight broadening of the signals being observed. Thermal vibrations of the coordinated ligand at the elevated temperature would explain the observed broadening and shifts of the ^{1}H resonance signals.

X-ray Structures of [Ga(Clbbpen)]ClO$_4$ and [In(Clbbpen)]ClO$_4$. Crystals of [Ga(**Clbbpen**)]ClO$_4$ suitable for crystallographic analysis were grown from a methanol solution by slow evaporation of the solvents at room temperature. An ORTEP drawing of [Ga(**Clbbpen**)]ClO$_4$ is shown in Figure 2; selected bond lengths and bond angles are listed in Table 6. In the triclinic unit cell, there are two [Ga(**Clbbpen**)]ClO$_4$ molecules, *e.g.* a pair of enantiomers. As expected, the Ga^{3+} ion was coordinated to the **bbpen**$^{2-}$ ligand via two amine nitrogen atoms, two pyridyl nitrogen atoms, and two anionic phenolate oxygen atoms to form a $N_2N'_2O_2$ donor set, giving monocationic complexes with a distorted octahedral geometry. The donor atoms N1, N3, O1 occupied one face of the octahedron while N2, N4, O2 occupied the other face. The two amine nitrogen atoms of the ethylenediamine backbone were coordinated cis to each other while the two pyridyl nitrogen atoms were coordinated trans to each other. The two phenolate oxygen atoms formed an equatorial plane with the amine nitrogen atoms and were coordinated cis to each other.

The three trans angles, N2−Ga−O1, N1−Ga−O2, and N3−Ga−N4, were 170.22(7), 169.67(7), and 165.83(7)°, respectively. The last angle had the largest deviation from 180° (~15°), probably caused by the intrinsically small bite angle of the two five-membered chelate rings. The other two trans angles, N2−Ga−O1 and N1−Ga−O2, which each involved one five-membered and one six-membered chelate ring, deviated less from 180°. The cis N−Ga−N′ angles within the two five-membered chelate rings, N2−Ga−N4 and N1−Ga−N3, were 79.72(7) and 78.82(7)°, respectively. The cis angle (N1−Ga−

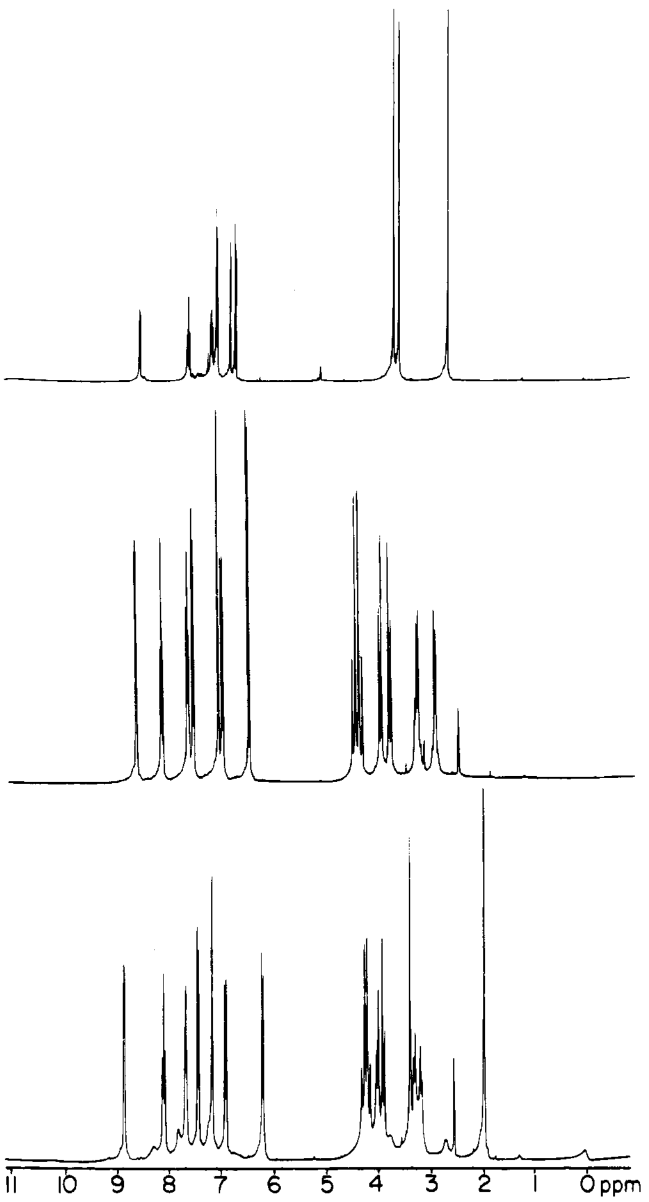


Figure 1. ^{1}H NMR spectra (300 MHz) of H_2**Clbbpen** (top, in $CDCl_3$), [Ga(**Clbbpen**)]ClO_4 (middle, in DMSO-d_6), and [In(**Clbbpen**)]ClO_4 (bottom, in DMSO-d_6).

N2) formed by the coordination of the two amine nitrogens was 82.81(7)°. Most of the N−Ga−O angles were in the range 91−93°. The only two exceptions were the angles N3−Ga−O1 and N4−Ga−O2, which were 96.03(7) and 97.92(7)°, respectively. N−Ga−N′ angles between different chelate rings (N2−Ga−N3 and N1−Ga−N4) were ~90°.

The two Ga−O bond lengths were 1.860(2) Å (Ga−O1) and 1.871(2) Å (Ga−O2). Ga−N1 and Ga−N2 bond lengths (Ga to amine nitrogen bond lengths) were 2.180(2) and 2.158(2) Å, respectively. Bond lengths of 2.121(2) and 2.107(2) Å were observed for the Ga−N3 and Ga−N4 bonds (Ga to pyridyl nitrogen bonds). The bond lengths of Ga to the phenolate oxygen and Ga to the amine nitrogen atom were comparable with bond lengths observed in Ga amine phenol,[2−5] Ga Schiff base,[30] and other hexacoordinated Ga complexes.[31−34] Bond lengths of Ga to the pyridyl nitrogen atom were consistent with bond lengths observed in Ga complexes involving heterocyclic ligands.[33−38]

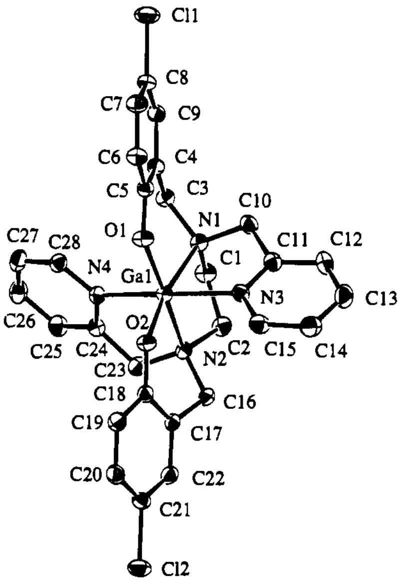


Figure 2. ORTEP drawing of the [Ga(**Clbbpen**)]$^+$ cation in [Ga(**Clbbpen**)]Cl_4 showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 33% probability level.

[In(**Clbbpen**)]ClO_4 crystals suitable for crystallographic analysis were obtained from a methanol solution by slow evaporation of solvent at room temperature. An ORTEP drawing of [In(**Clbbpen**)]ClO_4 is illustrated in Figure 3; selected bond lengths and bond angles are listed in Table 8. In each monoclinic unit cell, there are four [In(**Clbbpen**)]ClO_4 molecules, *e.g.* two pairs of enantiomers. The In^{3+} ion was also hexacoordinated by an $N_2N'_2O_2$ donor set, giving a monocationic complex. The distorted octahedral coordination geometry in [In(**Clbbpen**)]ClO_4 is very similar to the coordination geometry in [Ga(**Clbbpen**)]ClO_4. Two amine nitrogen and two phenolate oxygen atoms formed the equatorial plane of the octahedral geometry, where atoms of the same type were coordinated cis to each other. The two pyridyl nitrogen atoms, mutually trans, occupied the axial positions of the distorted octahedral geometry. One face of the octahedron was again occupied by N1, N3, O1 while the other face was occupied by N2, N4, O2, and the In−N and In−O bond lengths were consisted with those observed in hexadentate In amine phenol complexes.[2−5]

As in [Ga(**Clbbpen**)]ClO_4, the In^{3+} ion in [In(**Clbbpen**)]ClO_4 was coordinated in a distorted octahedral geometry; however, a greater degree of distortion was observed in the coordination geometry of [In(**Clbbpen**)]ClO_4. The trans angles N1−In−O2 and N2−In−O1 in [In(**Clbbpen**)]ClO_4 were 158.25(7) and 160.00(8)°, respectively. The deviations from 180° for these angles were ~20°, greater than that observed in [Ga(**Clbbpen**)]ClO_4; however, the trans angle N3−In−N4 was 166.69(7), close to that in [Ga(**Clbbpen**)]ClO_4 (165.83(7)°). The constraint of the two five-membered chelate rings associated with the N3−

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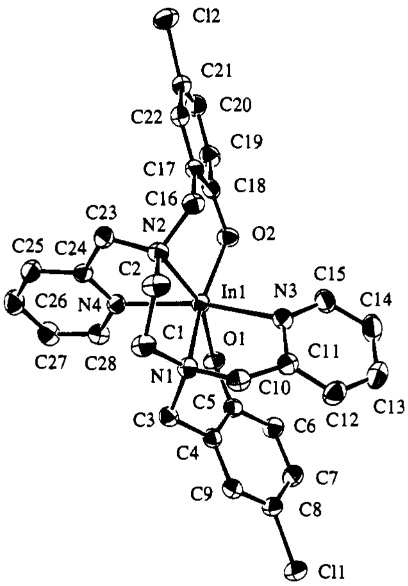
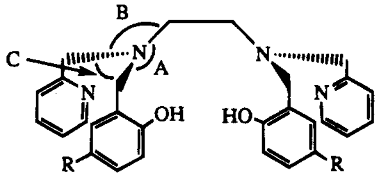


Figure 3. ORTEP drawing of the [In(**Clbbpen**)]$^+$ cation in [In(**Clbbpen**)]ClO$_4$ showing the crystallographic numbering. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 33% probability level.

Chart 2



M−N4 (M = Ga, In) angle most likely forced the N3−M−N4 angle to remain at ~166°. Larger deviations in the cis N−M−N′ angles were also observed in [In(**Clbbpen**)]ClO$_4$ compared to [Ga(**Clbbpen**)]ClO$_4$. An average deviation from 90° of ~13° was observed for the cis N−In−N′ angles, while the corresponding N−Ga−N′ angles only had an average deviation of ~4°. Another example of the greater distortion in the octahedral geometry of the In complex was the fact that the O1−In−O2 angle was 105.54(7)° while the corresponding O1−Ga−O2 angle was only 95.17(6)°. The greater distortion in the octahedral geometry of [In(**Clbbpen**)]ClO$_4$ versus [Ga(**Clbbpen**)]ClO$_4$ likely results from the six-coordinate ionic radius of In^{3+} (0.80 Å) being greater than that for Ga^{3+} (0.62 Å).

Since the In^{3+} ion is larger than the Ga^{3+} ion, it was expected that the angles associated with the pendant arms (angles A, B, and C in Chart 2) would be different for the [Ga(**Clbbpen**)]ClO$_4$ complex and the [In(**Clbbpen**)]ClO$_4$ complex. However, no significant difference was observed between the three angles in [Ga(**Clbbpen**)]ClO$_4$ and the corresponding angles in [In(**Clbbpen**)]ClO$_4$. For [In(**Clbbpen**)]ClO$_4$, the average angles for A, B, and C were 112.0, 110.4, and 111.1°, respectively. The average angles for A, B, and C in the [Ga(**Clbbpen**)]ClO$_4$ complex were 110.7, 110.1, 109.4°, respectively. These angles show very little deviation from tetrahedral values (within the experimental error). The close similarities of angles A, B, and C in both the Ga and In complexes suggest that, though greater distortion was observed in the octahedral geometry of [In(**Clbbpen**)]ClO$_4$, the cavity that is formed by the four pendant arms is sufficiently large to encapsulate ions as large as In^{3+} (0.80 Å),[39] without causing significant strain to the backbone of the ligand.

The distorted octahedral coordination geometries in [Ga(**Clbbpen**)]ClO$_4$ and [In(**Clbbpen**)]ClO$_4$ were consistent with the coordination environments in [Mn$^{\text{III}}$(**bbpen**)]PF$_6$[22] and [V$^{\text{III}}$(**bbpen**)]PF$_6$.[23] This is not surprising considering that six-coordinate ionic radii of V^{3+} (0.640 Å)[39] and high-spin Mn^{3+} (0.645 Å)[39] are very similar to the ionic radius of Ga^{3+} (0.62 Å).[39] The bond angles and bond lengths in these Mn$^{\text{III}}$ and V$^{\text{III}}$ complexes were consistent with those in the Ga and In complexes.

Concluding Remarks. A series of Ga and In complexes with **bbpen**$^{2-}$, **Clbbpen**$^{2-}$, and **Brbbpen**$^{2-}$ were prepared and characterized as monocationic complexes with the metal ion coordinated by a N$_2$N′$_2$O$_2$ donor set. Crystallographic analyses of [Ga(**Clbbpen**)]ClO$_4$ and [In(**Clbbpen**)]ClO$_4$ showed the metal ions to be coordinated by two amine nitrogen, two pyridyl nitrogen, and two anionic phenolate oxygen atoms in a distorted octahedral geometry. ^{1}H NMR spectral data for the Ga and In complexes showed rigid solution structures; no fluxional behavior was observed for these complexes at temperature as high as 120 °C.

That **bbpen**$^{2-}$ and its substituted analogs can form stable hexadentate complexes with both Ga^{3+} and In^{3+} suggests that the cavity formed by the two methylpyridyl and the two hydroxylbenzyl pendant groups is suitable for metal ions whose ionic radii are within the range of ~0.6−0.80 Å. This augers well for the coordination chemistry with tri- or tetravalent metal ions whose six-coordinate ionic radii are similar to the radii of Ga^{3+} and In^{3+} ions. Trivalent Mn (0.645 Å)[39] and V (0.640 Å)[39] complexes[22,23] with H$_2$**bbpen** have been reported. Preliminary investigation into the coordination of Tc^{3+} and Re^{3+} ions to H$_2$**bbpen** and its substituted analogs has shown that Tc and Re complexes with these ligands are possible.[40] Al complexes with H$_2$**bbpen**, H$_2$**Brbbpen**, and H$_2$**Clbbpen** were found to be much less stable than the Ga or In congeners, suggesting that H$_2$**bbpen**, H$_2$**Brbbpen**, and H$_2$**Clbbpen** may not be suitable for smaller metal ions such as Al^{3+}, which has a six-coordinate ionic radius of 0.53 Å.[39] Conversely it would be interesting to see if coordination of these ligands to larger metal ions (metal ions whose ionic radii is greater than 0.8 Å) would result in stable hexacoordinated mononuclear metal complexes.

The aqueous solution chemistry of sulfonated H$_2$**bbpen** and its Ga and In complexes is being studied and will be reported later.[41] The results suggest that H$_2$**bbpen** is thermodynamically competitive with transferrin for Ga^{3+} and In^{3+} metal ions.

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Supplementary Material Available: Complete tables of crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, and bond angles for both structures and additional tables of NMR data (19 pages). Ordering information is given on any current masthead page.

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