Coordination Chemistry of 2-(2′-Hydroxyphenyl)-2-oxazolines with Aluminum, Gallium, and Indium: First Tris(ligand)metal(III) Complexes of This Naturally Occurring Binding Group

H. R. Hoveyda, Veranja Karunaratne, Steven J. Rettig, and Chris Orvig*

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

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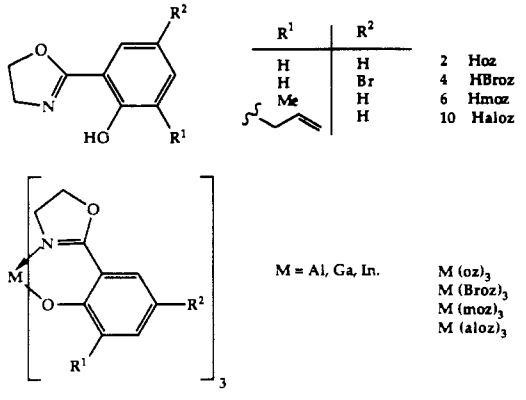
A series of tris(ligand)metal(III) complexes of group 13 metals (Al, Ga, In) with 2-(2′-hydroxyphenyl)-2-oxazoline (Hoz), 2-(5′-bromo-2′-hydroxyphenyl)-2-oxazoline (HBroz), 2-(2′-hydroxy-3′-methylphenyl)-2-oxazoline (Hmoz), 2-(2′-hydroxy-3′-allylphenyl)-2-oxazoline (Haloz) have been prepared. These compounds have been studied by a variety of techniques including variable-temperature NMR (^{1}H and ^{27}Al) and single-crystal X-ray diffraction. The M(oz)$_3$·CH$_3$OH complexes (M = Al, Ga, In) are isomorphous and isostructural. Crystallographic data for $C_{28}H_{28}MN_3O_7$: monoclinic, a = 12.0421 (9), 12.010 (3), 11.916 (2) Å; b = 13.421 (1), 13.427 (6), 13.526 (3) Å; c = 16.2308 (6), 16.328 (2), 16.845 (1) Å; β = 96.885 (5), 97.37 (1), 100.867 (8)°; V = 2604.2 (3), 2611 (1), 2666.4 (7) Å^3 (respectively for M = Al, Ga, In); Z = 4, space group $P2_1/n$. Crystallographic data for Al(moz)$_3$: $C_{30}H_{30}AlN_3O_6$, monoclinic, a = 11.096 (1) Å, b = 26.446 (1) Å, c = 9.620 (1) Å, β = 99.033 (8)°, V = 2788.0 (4) Å^3, Z = 4, space group Cc. Crystallographic data for Ga(aloz)$_3$: $C_{36}H_{36}GaN_3O_6$, monoclinic, a = 23.860 (2) Å, b = 12.123 (2) Å, c = 23.204 (2) Å, β = 95.041 (6)°, V = 6686 (2) Å^3, Z = 8, space group $C2/c$. The structures were solved by heavy-atom methods and were refined by full-matrix least-squares procedures to R = 0.041, 0.034, 0.030, 0.026, and 0.037 for 3670, 3384, 5762, 2753, and 3686 reflections with $I \geq 3\sigma(I)$, respectively. Both the solid-state and solution characterization of all the complexes revealed that the coordination geometry about the hexacoordinated metal center is *mer*. The temperature-dependent solution behavior was assigned to an interconversion of *mer* geometries about the metal center. As an example, the M(moz)$_3$ (M = Al, Ga, In) complexes were chosen, ^{1}H NMR coalescence temperatures were measured, and $\Delta G^{\ddagger}$ for the corresponding interconversion processes were calculated. The rates of interconversion correlate well with the ionic radii of the metals increasing in magnitude from M = Al to Ga to In.

Introduction

In a continuation of our interest in the coordination chemistry of group 13 (IIIA) metal ions, we have prepared a series of tris(oxazolinato)metal complexes. The ligands used in this study—2-(2′-hydroxyphenyl)-2-oxazoline, and a few substituted derivatives—act as bidentate monobasic ligands to form neutral complexes of Al(III), Ga(III), and In(III). Such metal complexes are of biomedical interest because of the association of Al with a variety of neurological dysfunctions and bone disorders, and because of the viability of radioisotopes of Ga (^{67}Ga, ^{68}Ga) and In (^{111}In, ^{113m}In) in the field of nuclear medicine.[1] To this end, they can act so as to increase the mobility and availability of these metal ions in vivo.



Significantly, the 2-(2′-hydroxyphenyl)-2-oxazoline ligating moiety is naturally occurring, and is found in certain classes of microbial iron chelators, the siderophores.[2] The high affinity of the siderophores for Fe(III) is due to the chemical nature of the chelating functionalities that evolution has favored over millions of years. These are usually catecholate[3] and hydroxamate[4] or, less frequently, 2-(2′-hydroxyphenyl)-2-oxazolinate residues. For example, in mycobactin, two hydroxamate residues (one cyclic, one acyclic) and a 2-(2′-hydroxyphenyl)-2-oxazolinate residue act in concert to form an extremely stable iron(III) complex.[5]

Given the similarities between the coordination requirements of Fe(III) and those of the group 13 metal ions, we have adopted a retro biomimetic approach: using simple bidentate 2-(2′-hydroxyphenyl)-2-oxazolines to investigate the relevance of this ligating functionality toward formation of neutral group 13 metal complexes. There is a paucity of structural information pertaining to the coordination geometry of 2-(2′-hydroxyphenyl)-2-oxazolinato metal complexes. To date, there exist only a few recent examples of structurally characterized bis(ligand)metal(II) complexes of similar 2-(2′-hydroxyphenyl)-2-oxazoline derived ligand systems with Co, Ni, and Zn,[6] as well as two Tc(V) complexes

* To whom correspondence should be addressed.

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of 2-(2′-hydroxyphenyl)benzothiazole.[7] In addition, Raymond et al. have recently characterized Cr(III) and Co(III) complexes of desferriferrithiocin, a tridentate analog.[8] Hence, this work presents the first structurally characterized tris(ligand) complexes of trivalent metal ions with the naturally occurring 2-(2′-hydroxyphenyl)-2-oxazolinate ligating moiety.

Experimental Section

Materials and Methods. All chemicals were reagent grade and were used as received unless otherwise specified: $In(NO_3)_3 \cdot 5H_2O$ (Aldrich), $Ga(NO_3)_3 \cdot 9H_2O$ (Alfa), $Al(NO_3)_3 \cdot 9H_2O$ and 2-aminoethanol (Mallinckrodt), $AlCl_3 \cdot 6H_2O$ and thionyl chloride (BDH), 1,1′-carbonyldiimidazole and 2-hydroxy-3-methylbenzoic acid (Sigma), and ethyl salicylate and 5-bromo-2-hydroxybenzoic acid (Aldrich). THF and diethyl ether were distilled from Na/benzophenone ketyl under Ar prior to use; CH_2Cl_2 was distilled over CaH_2 under Ar. Water was deionized (Barnstead D8902 and D8904 cartridges) and distilled (Corning MP-1 Megapure still). The yields reported refer to the isolated yields.

Instrumentation. NMR spectra were recorded on Bruker AC-200E (^1H, 200 MHz; ^{13}C, 50 MHz), Varian XL-300 (^1H, 300 MHz), and Bruker WH-400 (^1H, 400 MHz) instruments. ^1H NMR data are reported as δ from external TMS at 200 MHz in DMSO-d_6 unless otherwise stated. Infrared spectra were recorded either on a neat sample using NaCl windows (for liquid samples), or as KBr disks, in the range 4000–400 cm^{-1} on a Perkin-Elmer PE783 spectrophotometer and were referenced to polystyrene. Mass spectra were obtained with a Kratos MS 50 (electron-impact ionization, EI). Appropriate isotope ratios for all Br- and/or Ga-containing compounds were observed; only the most intense peaks are listed. Melting points were measured on a Mel-Temp apparatus and are uncorrected. Analyses for C, H, N, and Br were performed in this department on a Carlo Erba instrument.

^{27}Al NMR Spectroscopy. Spectra were recorded in DMSO and in DMF on a Varian XL-300 spectrometer operating at 78.16 MHz and accumulating 3500 transients with a pulse width of 15 μs and a spectral window of 37 kHz. All spectra were referenced to 0.20 M $Al(ClO_4)_3$ in 0.10 M $HClO_4$ with D_2O added as a lock signal, and downfield shifts are positive. The background correction was done for each spectrum by subtracting a spectrum run under identical conditions with the solvent.[9] For the variable-temperature experiments, 0.1 M $Al(ClO_4)_3$ in DMF was run as a control. The ^{27}Al NMR values reported in the experimental section are those obtained in DMSO; for the corresponding values obtained in DMF, see Table VII.

Ligand Syntheses. 2-Hydroxy-*N*-(2′-hydroxyethyl)benzamide (1). A modified literature preparation was used.[10] Ethyl salicylate (45.7 g, 0.28 mol) and 2-aminoethanol (16.7 g, 0.27 mol) were refluxed together neat for 2.5 h, and the resulting EtOH was removed under reduced pressure. The residue thus obtained was subjected to column chromatography on silica gel (eluant, 30% EtOAc in CH_2Cl_2) to elute the impurities. It was subsequently eluted with 25:5:70 EtOAc–CH_3OH–CH_2Cl_2 to afford 34 g (70%) of **1** as a white crystalline solid, mp 109–110 °C. ^1H NMR: 3.35 (t, 2H, J = 6 Hz), 3.50 (t, 2H, J = 6 Hz), 4.80 (broad s, 1H), 6.86 (t, 1H, J = 8 Hz), 6.88 (d, 1H, J = 8 Hz), 7.40 (t, 1H, J = 8 Hz), 7.85 (d, 1H, J = 8 Hz), 8.8 (broad s, 1H), 12.6 (broad s, 1H). IR (cm^{-1}, KBr disk): 3410 (ν_{O-H}), 3310 (ν_{N-H}), 1630 ($\nu_{C=O}$), 1590 ($\nu_{C=C\ aromatic}$), 1550, 1230, 1070, 1055, 755. Exact mass calcd (found) for $C_9H_{11}NO_3$: 181.0733 (181.0739).

2-(2′-Hydroxyphenyl)-2-oxazoline (Hoz) (2). A published procedure was modified.[10] Thionyl chloride (6.69 g, 0.06 mol) was slowly added to a solution of **1** (5.2 g, 0.03 mol) in CH_2Cl_2 (150 mL) under Ar at 0 °C. The reaction was allowed to warm up gradually to room temperature, and was left stirring under Ar for 18 h. The **2**·HCl salt was then filtered out (5.7 g, 95%), made basic with saturated aqueous $NaHCO_3$, and extracted with diethyl ether (15 × 50 mL). The ether extracts were combined, dried ($MgSO_4$), and concentrated under reduced pressure to give a reddish oil which solidified upon drying in vacuo, affording a faintly pink solid (3.6 g, 81% based on **2**·HCl), mp 36–37 °C (lit. mp 37–40 °C).[10] ^1H NMR: 4.08 (t, 2H, J = 8 Hz), 4.50 (t, 2H, J = 8 Hz), 6.90–7.04 (m, 2H), 7.45 (t, 1H, J = 6 Hz), 7.62 (d, 1H, J = 6 Hz), 12.20 (s, 1H). IR (cm^{-1}, KBr disk): 1640 ($\nu_{C=N}$), 1620 ($\nu_{C=C\ aromatic}$), 1490, 1370, 1260, 1230, 1065, 940, 710. MS (EI): m/z 163 (M^+). Anal. Calcd (found) for $C_9H_9NO_2$: C, 66.23 (66.35); H, 5.56 (5.49); N, 8.58 (8.56).

5-Bromo-2-hydroxy-*N*-(2′-hydroxyethyl)benzamide (3). To a solution of 5-bromo-2-hydroxybenzoic acid (6.0 g, 0.028 mol) in THF (200 mL) was added 1,1′-carbonyldiimidazole (5.4 g, 0.033 mol) under N_2. The resulting mixture was refluxed for an hour, whereupon 2-aminoethanol (3.3 g, 0.055 mol) was added dropwise, and the reaction mixture was refluxed for 18 h under N_2. The residue obtained after removal of solvent was subjected to column chromatography on silica gel (elution with diethyl ether:pentane, 4:1). Concentration of the appropriate fractions furnished 4.4 g (60%) of **3** as a colorless oil. ^1H NMR: 3.35 (m, 2 H), 3.90 (m, 2 H), 4.80 (t, 1H, J = 6 Hz), 6.90 (d, 1H, J = 8 Hz), 7.55 (dd, 1H, J = 8, 2 Hz), 8.10 (d, 1H, J = 2 Hz), 8.90 (broad s, 1H), 12.60 (broad s). IR (cm^{-1}, KBr disk): 3480 (ν_{O-H}), 3330 (ν_{N-H}), 1645 ($\nu_{C=O}$), 1590 and 1550 ($\nu_{C=C}$), 1230, 1060, 820. MS (EI): m/z 259 (M^+ ^{79}Br), 261 (M^+ ^{81}Br).

2-(5′-Bromo-2′-hydroxyphenyl)-2-oxazoline (HBroz) (4). HBroz was prepared by a method similar to that of Hoz, by using **3**, in 91% yield as a white crystalline solid, mp 119–120 °C. ^1H NMR (δ at 200 MHz in $CDCl_3$): 4.15 (t, 2H, J = 8 Hz), 4.42 (t, 2H, J = 8 Hz), 6.85 (d, 1H, J = 9 Hz), 7.45 (d, 1H, J = 9 Hz), 7.75 (s, 1H), 12.18 (s, 1H). ^{13}C NMR (δ at 50 MHz in DMSO-d_6): 53.12, 67.49, 109.72, 112.14, 119.01, 129.72, 136.17, 158.37, 164.42. IR (cm^{-1}, KBr disk): 1640 ($\nu_{C=N}$), 1620 ($\nu_{C=C\ aromatic}$), 1470, 1360, 1295, 1250, 1230, 935, 825. MS (EI): m/z 241 (M^+). Anal. Calcd (found) for $C_9H_8BrNO_2$: C, 44.66 (44.60); H, 3.33 (3.28); N, 5.79 (5.70).

2-Hydroxy-3-methyl-*N*-(2′-hydroxyethyl)benzamide (5). Compound **5** was prepared by a method analogous to that of **3**, by utilizing 2-hydroxy-3-methylbenzoic acid, in 81% yield as a yellowish oil. ^1H NMR: 2.15 (s, 3H), 3.40 (m, 2H), 3.55 (m, 2H), 4.85 (broad s, 1H), 6.78 (t, 1H, J = 6 Hz), 7.30 (d, 1H, J = 6 Hz), 7.70 (d, 1H, J = 6 Hz), 8.90 (broad s, 1H), 13.25 (broad s, 1H). IR (cm^{-1}, neat): 3350 (ν_{O-H}), 3090 (ν_{N-H}), 1630 ($\nu_{C=O}$), 1608, 1585 ($\nu_{C=C\ aromatic}$), 1540, 1250, 1050, 750. Exact mass calcd (found) for $C_{10}H_{13}NO_3$: 195.0896 (195.0895).

2-(2′-Hydroxy-3′-methylphenyl)-2-oxazoline (Hmoz) (6). Hmoz was prepared in analogous fashion to Hoz, by using **5** (in ether), in 70% yield as a pink solid, mp 54–55 °C. ^1H NMR (δ at 400 MHz in DMSO-d_6): 2.21 (s, 3H), 4.07 (t, 2H, J = 8 Hz), 4.47 (t, 2H, J = 8 Hz), 6.84 (t, 1H, J = 8 Hz), 7.32 (d, 1H, J = 8 Hz), 7.47 (d, 1H, J = 8 Hz), 12.46 (s, 1H). IR (cm^{-1}, KBr disk): 1640 ($\nu_{C=N}$), 1620 ($\nu_{C=C}$), 1460, 1370, 1305, 1270, 1145, 960, 750. Exact mass calcd (found) for $C_{10}H_{11}NO_2$: 177.0783 (177.0790). Anal. Calcd (found) for $C_{10}H_{11}NO_2$: C, 67.78 (67.36); H, 6.26 (6.13); N, 7.90 (7.78).

Ethyl (2-allyloxy)salicylate (7). This compound was prepared by analogy to a literature procedure.[11] A mixture of 54.8 g (0.33 mol) ethyl salicylate, 200 mL of acetone, 57.2 mL (0.66 mol) of allyl bromide, and 91.22 g (0.66 mol) of potassium carbonate was heated to reflux for 72 h under N_2. After cooling, filtering out of the potassium carbonate, and evaporation of the solvent, the oily residue was taken up in diethyl ether, washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give the crude product. Column chromatography on silica gel (eluant, pentane–ether, 1:1) afforded the pure allyl ether as a pale yellow oil (47.8 g, 70%). ^1H NMR: 1.3 (t, 3H, J = 8 Hz), 4.25 (q, 2H, J = 8 Hz), 4.62 (d, 2H, J = 3 Hz), 5.25 (d, 1H, J = 10 Hz), 5.50 (d, 1H, J = 15 Hz), 5.95–6.15 (m, 1H), 7.02 (t, 1H, J = 6 Hz), 7.15 (d, 1H, J = 6 Hz), 7.50 (t, 1H, J = 6 Hz), 7.65 (d, 1H, J = 6 Hz).

Ethyl (3-allyl-2-hydroxy)salicylate (8). The allyl ether **7** (47.8 g, 0.23 mol) was heated under N_2 at reflux for 18 h, to yield pure **8** quantitatively. The compound was used in the next step without further purification. ^1H NMR (δ at 200 MHz in $CDCl_3$): 1.40 (t, 3H, J = 8 Hz), 3.40 (d, 2H, J = 5 Hz), 4.40 (q, 2H, J = 8 Hz), 5.00 (m, 1H), 5.15 (m, 1H), 5.90–6.15 (m, 1H), 6.82 (t, 1H, J = 6 Hz), 7.35 (d, 1H, J = 6 Hz), 7.75 (d, 1H, J = 6 Hz), 11.15 (s, 1H).

3-Allyl-2-hydroxy-*N*-(2′-hydroxyethyl)benzamide (9). Compound **9** was prepared by a method analogous to that for **1**, by using **8**, in 87% yield as a yellowish oil after column chromatography on silica gel (eluant, diethyl ether). ^1H NMR (δ at 300 MHz in DMSO-d_6): 3.20–3.46 (m, 4H), 3.58–3.63 (m, 2H), 4.88, 5.03 (two m, 2H), 5.08 (s, 1H), 5.92–6.04 (m, 1H), 6.85 (t, 1H, J = 6 Hz), 7.27 (d, 1H, J = 6 Hz), 7.77 (d, 1H, J = 6 Hz), 8.88 (broad s, 1H), 13.38 (s, 1H). IR (cm^{-1}, neat): 3370

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(ν_{O-H}), 3090 (ν_{N-H}), 1630 ($\nu_{C=O}$), 1605, 1585 ($\nu_{C=C\ aromatic}$), 1540, 1250, 1065, 750. Exact mass calcd (found) for $C_{12}H_{15}NO_3$: 221.1054 (221.1056).

2-(2′-Hydroxy-3′-allylphenyl)-2-oxazoline (Haloz) (10). To a solution of **9** (5.8 g, 26.24 mmol) in diethyl ether (120 mL) at 0 °C, under Ar, was slowly added 6 mL (81 mmol) of thionyl chloride. The resulting mixture was allowed to warm up to room temperature, while being stirred under Ar for a further 18 h. Filtration furnished **10**·HCl (6.3 g, 98%) which was made basic with saturated aqueous $NaHCO_3$ and extracted into ether to yield a reddish oil upon removal of solvent as pure product (3.7 g, 70%). ^{1}H NMR (δ at 400 MHz in $CDCl_3$): 3.45 (d, 2H, J = 5 Hz), 4.10 (t, 2H, J = 10 Hz), 4.40 (t, 2H, J = 10 Hz), 5.08 (d, 1H, J = 5 Hz), 5.12 (d, 1H, J = 15 Hz), 5.95–6.18 (m, 1H), 6.80 (t, 1H, J = 6 Hz), 7.25 (d, 1H, J = 6 Hz), 7.55 (d, 1H, J = 6 Hz), 12.45 (s, 1H). IR (cm^{-1}, neat): 1635 ($\nu_{C=N}$), 1480, 1450, 1370, 1315, 1260, 1130, 960, 750. Exact mass calcd (found) for $C_{12}H_{13}NO_2$: 203.0944 (203.0946).

Metal Complex Syntheses. Tris[2-(2′-hydroxyphenyl)-2-oxazolinato]-indium(III)–Methanol, In(oz)$_3$·CH$_3$OH. To a solution of Hoz (0.216 g, 1.32 mmol) in CH_3OH (40 mL) was added $In(NO_3)_3$·5H_2O (0.150 g, 0.38 mmol) in 11 mL of CH_3OH–H_2O (10:1), followed by slow addition of 3.3 equiv of NaOH (1 M). Large yellow-orange crystals of In(oz)$_3$·CH_3OH suitable for X-ray crystallography were obtained by slow evaporation, at room temperature over a period of ca. 10 days to afford a (combined) yield of 0.24 g (100%) as a light-pink solid, mp 290–292 °C. ^{1}H NMR: 3.85 (t, 2H, J = 10 Hz), 4.46 (t, 2H, J = 10 Hz), 6.50 (t, 1H, J = 8 Hz), 6.63 (d, 1H, J = 8 Hz), 7.25 (t, 1H, J = 8 Hz), 7.60 (d, 1H, J = 8 Hz). IR (cm^{-1}, KBr disk): 1620 ($\nu_{C=N}$), 1590 ($\nu_{C=C\ aromatic}$), 1470, 1440, 1390, 1340, 1230, 1160, 1070, 950, 930, 855, 760, 695, 658, 560. MS (EI): m/z 163 (L^+), 277 (ML^+), 439 (ML_2^+), 601 (ML_3^+). Anal. Calcd (found) for $C_{28}H_{28}InN_3O_7$: C, 53.10 (53.00); H, 4.46 (4.40); N, 6.63 (6.56).

Tris[2-(2′-hydroxyphenyl)-2-oxazolinato]gallium(III)–Methanol, Ga(oz)$_3$·CH$_3$OH. A preparation analogous to that for In(oz)$_3$ with $Ga(NO_3)_3$·9H_2O (0.158 g, 0.38 mmol), Hoz (0.208 g, 1.28 mmol), and 3.3 equiv of NaOH (1 M) in 50 mL CH_3OH–H_2O (10:1) yielded 0.184 g (82%) of a light-pink crystalline solid, mp 273–274 °C. X-ray quality crystals were obtained by slow evaporation at room temperature over a period of two weeks. ^{1}H NMR: 3.45–3.85, 3.85–4.22 (two broad s, 2H), 4.36–4.54 (m, 2H), 6.48 (m, 2H), 7.18 (t, 1H, J = 6 Hz), 7.50 (d, 1H, J = 6 Hz). IR (cm^{-1}, KBr disk): 1620 ($\nu_{C=N}$), 1545, 1470, 1445, 1395, 1342, 1240, 1155, 1073, 930, 850, 760, 692, 660, 568. MS (EI): m/z 163 (L^+), 231 (ML^+ ^{69}Ga), 393 (ML_2^+ ^{69}Ga), 555 (ML_3^+ ^{69}Ga). Anal. Calcd (found) for $C_{28}H_{28}GaN_3O_7$: C, 57.17 (57.25); H, 4.80 (4.72); N, 7.14 (7.17).

Tris[2-(2′-hydroxyphenyl)-2-oxazolinato]aluminum(III)–Methanol, Al(oz)$_3$·CH$_3$OH. This compound was synthesized using a procedure similar to the preparation of In(oz)$_3$. $AlCl_3$·6H_2O (0.091 g, 0.38 mmol), Hoz (0.205 g, 1.26 mmol) and 3.3 equiv of 1 M NaOH in 50 mL of CH_3OH–H_2O (10:1) afforded Al(oz)$_3$ (0.14 g, 68%), by slow evaporation of solvent at room temperature as light-pink crystals, some of which were suitable for X-ray crystallography; mp 283–284 °C. ^{1}H NMR: 3.45–3.66, 3.92–4.18 (two m, 2H), 4.38–4.54 (m, 2H), 6.48 (m, 2H), 7.20 (m, 1H), 7.50 (m, 1H). IR (cm^{-1}, KBr disk): 1620 ($\nu_{C=N}$), 1550, 1470, 1450, 1395, 1345, 1250, 1245, 1152, 1070, 950, 945, 860, 760, 692, 666, 570. MS (EI): m/z 163 (L^+), 189 (ML^+), 351 (ML_2^+), 513 (ML_3^+). Anal. Calcd (found) for $C_{28}H_{28}AlN_3O_7$: C, 61.64 (61.72); H, 5.17 (5.14); N, 7.70 (7.74). ^{27}Al NMR: 8.2 ppm ($W_{1/2}$ = 1950 Hz).

Tris[2-(5′-bromo-2′-hydroxyphenyl)-2-oxazolinato]indium(III), In(Broz)$_3$. $In(NO_3)_3$·5H_2O (0.113 g, 0.29 mmol), HBroz (0.237 g, 9.8 mmol), and 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (70 mL, 10:1) afforded, after slow evaporation at room temperature, 0.192 g (79%) of In(Broz)$_3$ as a cream-colored solid, mp 279–281 °C. ^{1}H NMR: 3.95 (t, 2H, J = 10 Hz), 4.50 (t, 2H, J = 10 Hz), 6.60 (d, 1H, J = 10 Hz), 7.65 (s, 1H). IR (cm^{-1}, KBr disk): 1615 ($\nu_{C=N}$), 1585 ($\nu_{C=C\ aromatic}$), 1530, 1460, 1405, 1380, 1320, 1220, 1090, 1060, 940, 820, 700, 645, 580, 530. MS (EI): m/z 241 (L^+), 355 (ML^+), 597 (ML_2^+), 839 (ML_3^+). Anal. Calcd (found) for $C_{27}H_{21}Br_3InN_3O_6$: C, 38.70 (38.79); H, 2.53 (2.58); Br, 28.60 (28.44); N, 5.01 (4.96).

Tris[2-(5′-bromo-2′-hydroxyphenyl)-2-oxazolinato]gallium(III), Ga(Broz)$_3$. A solution of $Ga(NO_3)_3$·9H_2O (0.106 g, 0.25 mmol), HBroz (0.203 g, 0.84 mmol), and 3.3 equiv of 1 M NaOH in 70 mL of CH_3OH–H_2O (10:1) furnished, upon slow evaporation of CH_3OH solvent at room temperature, Ga(Broz)$_3$ (0.112 g, 57%) as a cream-colored solid, mp 258–259 °C. ^{1}H NMR: 3.45–3.85 (broad s, 1H, $W_{1/2}$ = 30 Hz), 3.85–4.25 (broad s, 1H, $W_{1/2}$ = 30 Hz), 4.35–4.70 (m, 2H, $W_{1/2}$ = 20 Hz), 6.50 (d, 1H, J = 8 Hz, $W_{1/2}$ = 20 Hz), 7.30 (d, 1H, J = 8 Hz, $W_{1/2}$ = 20 Hz), 7.54 (s, 1H, $W_{1/2}$ = 10 Hz). IR (cm^{-1}, KBr disk): 1625 ($\nu_{C=N}$), 1585 ($\nu_{C=C\ aromatic}$), 1535, 1460, 1415, 1390, 1330, 1230, 1090, 1075, 940, 830, 700, 650, 595, 530. MS (EI): m/z 241, 243 (L^+), 311 (ML^+), 551 (ML_2^+), 793 (ML_3^+). Anal. Calcd (found) for $C_{27}H_{21}Br_3GaN_3O_6$: C, 40.90 (40.83); H, 2.67 (2.69); Br, 30.23 (30.11); N, 5.30 (5.29).

Tris[2-(5′-bromo-2′-hydroxyphenyl)-2-oxazolinato]aluminum(III), Al(Broz)$_3$. $AlCl_3$·6H_2O (0.06 g, 0.25 mmol) was added to 0.200 g of HBroz (0.83 mmol) in the presence of 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (70 mL, 10:1) to yield Al(Broz)$_3$ (0.13 g, 67%) as a cream-colored solid, upon slow evaporation at room temperature; mp 217–219 °C. ^{1}H NMR: 3.20–3.40, 3.40–4.22 (two m, 2H, $W_{1/2}$ = 30 Hz), 4.35–4.70 (m, 2H, $W_{1/2}$ = 20 Hz), 6.50 (m, 1H, $W_{1/2}$ = 10 Hz), 7.30 (m, 1H, $W_{1/2}$ = 10 Hz), 7.54 (m, 1H, $W_{1/2}$ = 10 Hz). IR (cm^{-1}, KBr disk): 1630 ($\nu_{C=N}$), 1590 ($\nu_{C=C\ aromatic}$), 1540, 1470, 1420, 1390, 1330, 1240, 1090, 945, 830, 710, 660, 600, 535. MS (EI): m/z 241 (L^+), 268 (ML^+), 509 (ML_2^+), 749 (ML_3^+). Anal. Calcd (found) for $C_{27}H_{21}AlBr_3N_3O_6$: C, 43.23 (43.09); H, 2.82 (2.88); Br, 31.95 (31.80); N, 5.60 (5.54). ^{27}Al NMR: 11.4 ppm ($W_{1/2}$ = 2680 Hz).

Tris[2-(2′-hydroxy-3′-methylphenyl)-2-oxazolinato]indium(III), In(moz)$_3$. A solution of $In(NO_3)_3$·5H_2O (0.122 g, 0.313 mmol), Hmoz (0.183 g, 1.03 mmol), and 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (50 mL, 10:1) afforded In(moz)$_3$ (0.15 g, 74%) as a light-pink solid upon slow evaporation of the solvent at room temperature; mp 235–236 °C. ^{1}H NMR (δ at 300 MHz in DMSO-d_6): 2.00 (s, 3H), 3.96 (t, 2H, J = 9 Hz), 4.45 (t, 2H, J = 9 Hz), 6.39 (t, 1H, J = 8 Hz), 7.16 (d, 1H, J = 8 Hz), 7.40 (d, 1H, J = 8 Hz). IR (cm^{-1}, KBr disk): 1610 ($\nu_{C=N}$), 1590, 1552, 1450, 1425, 1385, 1330, 1240, 1145, 1085, 960, 860, 820, 750, 710, 640, 500. Exact mass calcd (found) for $C_{30}H_{30}InN_3O_6$: 643.1176 (643.1179). Anal. Calcd (found) for $C_{30}H_{30}InN_3O_6$: C, 64.86 (64.60); H, 5.44 (5.43); N, 7.56 (7.49).

Tris[2-(2′-hydroxy-3′-methylphenyl)-2-oxazolinato]gallium(III), Ga(moz)$_3$. A solution of $Ga(NO_3)_3$·9H_2O (0.134 g, 0.32 mmol), Hmoz (0.187 g, 1.06 mmol), and 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (50 mL, 10:1) furnished Ga(moz)$_3$ (0.19 g, 100%) as a light-pink solid upon slow evaporation of solvent at room temperature; mp 234–236 °C. ^{1}H NMR (δ at 300 MHz in DMSO-d_6): 1.48 (s, 3H, $W_{1/2}$ = 14 Hz), 2.07, 2.23 (pair of s, 6H, $W_{1/2}$ = 27 Hz), 3.53–4.70 (series of m, 12H), 6.30–6.57 (m, 3H), 6.90–7.60 (m, 6H). IR (cm^{-1}, KBr disk): 1625 ($\nu_{C=N}$), 1590 ($\nu_{C=C\ aromatic}$), 1560, 1450, 1430, 1390, 1330, 1250, 1145, 1085, 960, 860, 825, 750, 710, 615, 503. Exact mass calcd (found): for $C_{30}H_{30}{}^{69}GaN_3O_6$, 597.1393 (597.1396); for $C_{30}H_{30}{}^{71}GaN_3O_6$, 599.1385 (599.1388). Anal. Calcd (found) for $C_{30}H_{30}GaN_3O_6$: C, 60.23 (60.06); H, 5.05 (5.06); N, 7.02 (7.05).

Tris[2-(2′-hydroxy-3′-methylphenyl)-2-oxazolinato]aluminum(III), Al(moz)$_3$. A solution of $AlCl_3$·6H_2O (0.13 g, 0.34 mmol), Hmoz (0.199 g, 1.12 mmol), and 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (50 mL, 10:1) yielded Al(moz)$_3$ (0.135 g, 71%) as a light-pink solid after slow evaporation of solvent at room temperature; mp 240–241 °C. The same procedure also afforded light-pink crystals suitable for X-ray crystallography. ^{1}H NMR (δ at 300 MHz in DMSO-d_6): 1.44 (s, 3H), 2.05 (s, 3H), 2.12 (s, 3H), 3.55–4.60 (series of m, 12H), 6.34–6.58 (m, 3H), 7.04–7.42 (m, 6H). IR (cm^{-1}, KBr disk): 1625 ($\nu_{C=N}$), 1590 ($\nu_{C=C\ aromatic}$), 1560, 1460, 1400, 1330, 1290, 1280, 1250, 1170, 1150, 1085, 1005, 960, 880, 830, 750, 710, 680, 670, 510. Exact mass calcd (found) for $C_{30}H_{30}AlN_3O_6$: 555.1957 (555.1964). Anal. Calcd (found) for $C_{30}H_{30}AlN_3O_6$: C, 64.86 (64.60); H, 5.44 (5.43); N, 7.56 (7.49). ^{27}Al NMR: 8.1 ppm ($W_{1/2}$ = 1790 Hz).

Tris[2-(2′-hydroxy-3′-allylphenyl)-2-oxazolinato]indium(III), In(aloz)$_3$. $In(NO_3)_3$·5H_2O (0.225 g, 0.58 mmol) was added to Haloz (0.386 g, 1.9 mmol) and 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (50 mL, 10:1) to afford In(aloz)$_3$ (0.193 g, 47%) as a white solid upon slow evaporation of solvent at room temperature. The same procedure also furnished light-pink crystals suitable for X-ray crystallography, mp 173–174 °C. ^{1}H NMR: 3.20 (d, 2H, J = 5 Hz), 3.95 (t, 2H, J = 10 Hz), 4.45 (t, 2H, J = 10 Hz), 4.80–5.05 (m, 2H), 5.80–6.05 (m, 1H), 6.50 (t, 1H, J = 8 Hz), 7.12 (d, 1H, J = 8 Hz), 7.45 (d, 1H, J = 8 Hz). IR (cm^{-1}, KBr disk): 1610 ($\nu_{C=N}$), 1555 ($\nu_{C=C\ aromatic}$), 1440, 1385, 1245, 1145, 973, 755. MS (EI): m/z 203 (L^+), 317 (ML^+), 519 (ML_2^+), 721 (ML_3^+). Anal. Calcd (found) for $C_{36}H_{36}InN_3O_6$: C, 59.93 (59.92); H, 5.03 (4.99); N, 5.82 (5.82).

Tris[2-(2′-hydroxy-3′-allylphenyl)-2-oxazolinato]gallium(III), Ga(aloz)$_3$. $Ga(NO_3)_3$·9H_2O (0.237 g, 0.57 mmol) was added to Haloz (0.380 g, 1.87 mmol) and 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (50 mL, 10:1) to afford Ga(aloz)$_3$ (0.38 g, 66%) as a white solid upon slow

Table I. Selected Crystallographic Data for the Five Compounds[a]

compound	$Al(oz)_3 \cdot CH_3OH$	$Ga(oz)_3 \cdot CH_3OH$	$In(oz)_3 \cdot CH_3OH$	$Al(moz)_3$	$Ga(aloz)_3$
formula	$C_{28}H_{28}AlN_3O_7$	$C_{28}H_{28}GaN_3O_7$	$C_{28}H_{28}InN_3O_7$	$C_{30}H_{30}AlN_3O_6$	$C_{36}H_{36}GaN_3O_6$
fw	545.53	588.27	633.36	555.57	676.42
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	Cc	$C2/c$
a, Å	12.0421 (9)	12.010 (3)	11.916 (2)	11.096 (1)	23.860 (2)
b, Å	13.421 (1)	13.427 (6)	13.526 (3)	26.446 (1)	12.123 (2)
c, Å	16.2308 (6)	16.328 (2)	16.845 (1)	9.620 (1)	23.204 (2)
β, deg	96.885 (5)	97.37 (1)	100.867 (8)	99.033 (8)	95.041 (6)
V, Å^3	2604.2 (3)	2611 (1)	2666.4 (7)	2788.0 (4)	6686 (2)
Z	4	4	4	4	8
ρ_{calc}, g/cm^3	1.391	1.496	1.578	1.323	1.344
T, °C	21	21	21	21	21
radiation (λ, Å)	Cu (1.541 78)	Mo (0.710 69)	Mo (0.710 69)	Cu (1.541 78)	Cu (1.541 78)
μ, cm^{-1}	11.02	10.98	9.21	10.11	14.96
transm factors	0.93–1.00	0.96–1.00	0.94–1.00	0.83–1.00	0.93–1.00
R	0.041	0.034	0.030	0.026	0.037
R_w	0.048	0.034	0.031	0.030	0.038
gof	2.62	1.95	1.78	2.91	1.75

[a] Temperature 294 K, function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Values given for R, and R_w are based on those reflections with $I \geq 3\sigma(I)$, Rigaku AFC6S diffractometer, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B) + (pF^2)^2]/(Lp)^2$ (S = scan rate, C = scan count, B = normalized background count).

evaporation of solvent at room temperature; mp 290 °C dec. This procedure also yielded light-pink crystals suitable for X-ray crystallography. ^{1}H NMR: 3.20–3.40 (m, 2H), 3.60–3.75, 4.05–4.25 (two m, 2H), 4.40–4.55 (m, 2H), 5.55–6.05 (two m, 1H), 6.35–6.50 (m, 1H), 7.00–7.20 (m, 1H), 7.28–7.50 (m, 1H). IR (cm^{-1}, KBr disk): 1620 ($\nu_{C=N}$), 1555 ($\nu_{C=C}$), 1445, 1393, 1250, 1148, 975, 755. MS (EI): m/z 203 (L^+), 271 (ML^+), 473 (ML_2^+), 675 (ML_3^+). Anal. Calcd (found) for $C_{36}H_{36}GaN_3O_6$: C, 63.92 (63.72); H, 5.36 (5.37); N, 6.21 (6.18).

Tris[2-(2′-hydroxy-3′-allylphenyl)-2-oxazolinato]aluminum(III), Al(aloz)$_3$. $Al(NO_3)_3 \cdot 9H_2O$ (0.177 g, 0.47 mmol) was added to Haloz (0.137 g, 1.56 mmol) and 3.3 equiv of 1 M NaOH in CH_3OH–H_2O (50 mL, 10:1) to afford $Al(aloz)_3$ (0.14 g, 48%) as a white solid upon slow evaporation of solvent at room temperature, mp 330 °C dec. ^{1}H NMR: 3.10–3.35 (partially obscured m, 2H), 3.40–3.75 (m, 1H), 3.90–4.25 (m, 1H), 4.35–4.55 (m, 2H), 4.70–5.05 (m, 2H), 5.50–6.00 (two m, 2H), 6.40–6.52 (m, 1H), 7.05–7.18 (m, 1H), 7.30–7.45 (m, 1H). IR (cm^{-1}, KBr disk): 1625 ($\nu_{C=N}$), 1560 ($\nu_{C=C}$), 1450, 1395, 1257, 1147, 980, 755. MS (EI): m/z 203 (L^+), 229 (ML^+), 431 (ML_2^+), 633 (ML_3^+). Anal. Calcd (found) for $C_{36}H_{36}AlN_3O_6$: C, 68.24 (68.00); H, 5.73 (5.74); N, 6.63 (6.57). ^{27}Al NMR: 9.0 ppm ($W_{1/2}$ = 2150 Hz).

X-ray Crystallographic Analyses. Selected crystallographic data for $M(oz)_3 \cdot CH_3OH$ (M = Al, Ga, In), $Al(moz)_3$, and $Ga(aloz)_3$ appear in Table I. The final unit cell parameters were obtained by least-squares methods on the setting angles for 25 reflections with 2θ = 88.2–107.7, 30.4–36.0, 40.9–44.3, 97.1–112.9 and 49.6–60.1° for the five complexes, respectively. Data were collected on a Rigaku AFC6S diffractometer. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for all five compounds. The data were processed and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for four reflections).[12]

The structure analysis of $Al(moz)_3$ was initiated in the noncentrosymmetric space group Cc and that of $Ga(aloz)_3$ in the centrosymmetric space group $C2/c$. These choices were based on the E statistics and the Patterson functions and were confirmed by the subsequent successful solutions and refinements of the structures. The structures were solved by heavy-atom methods, the coordinates of the heavy atoms being determined from the Patterson functions and those of the remaining nonhydrogen atoms from subsequent difference Fourier syntheses. The structure analyses of $M(oz)_3 \cdot CH_3OH$ (M = Al and Ga) were initiated with the coordinates of the isomorphous and isostructural indium analog. The methanol solvate molecule in the $M(oz)_3 \cdot CH_3OH$ complexes shows decreasing magnitudes of thermal motion going from M = Al to Ga to In.

In $Ga(aloz)_3$ all three allyl groups were disordered. The C(10–12) allyl group was refined with a 2-fold disorder of the terminal carbon atom, the C(34–36) allyl with 2-fold disorder of both the β- and γ-carbon atoms, and the C(22–24) allyl group with a 3-fold disorder of the β-carbon and a 2-fold disorder of the terminal γ-carbon atom. Site occupancy parameters for the disordered carbon atoms were initially estimated from relative Fourier map peak heights and were adjusted as the refinement progressed to result in approximately equal thermal parameters for the multiple sites. Attempts to refine both the thermal parameters and the site occupancy factors did not yield satisfactory results. The thermal motion is substantial for the allyl groups in $Ga(aloz)_3$ and, in combination with the disorder, results in far from ideal geometry for these moieties. The remainder of the $Ga(aloz)_3$ molecule, however, is well-resolved.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The OH hydrogen atoms of the solvent molecules in $In(oz)_3 \cdot CH_3OH$ and $Ga(oz)_3 \cdot CH_3OH$ were included in difference map positions but were not refined (that for the aluminum complex could not be located) and all other hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{bonded\ atom}$), with the exception of some of those associated with the C(23B) components of the 3-fold disordered allyl group in $Ga(aloz)_3$. Corrections for secondary extinction were applied for $Al(oz)_3 \cdot CH_3OH$, $Al(moz)_3$, and $Ga(aloz)_3$, the final values of the extinction coefficients being 1.10×10^{-4}, 3.43×10^{-4}, and 1.20×10^{-5}, respectively. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 13. A parallel refinement of the structure of $Al(moz)_3$ having the opposite polarity[14] resulted in significantly higher residuals, the R and R_w ratios being 1.038 and 1.035, respectively.

Selected bond lengths appear in Tables II and III, and selected bond angles appear in Tables IV and V. Complete tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, bond distances, bond angles, hydrogen atom coordinates, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for each of the five structures are included as supplementary material (see paragraph at the end of the paper).

Results and Discussion

Ligands. The oxazoline ring system was first synthesized in 1884;[15] however, it has only been during the past 2 decades that the synthetic utility of oxazolines, particularly in the areas of asymmetric synthesis and enantioselective transition metal catalysis,[16] has been appreciated. Our interest in 2-(2′-hydroxyphenyl)-2-oxazolines stems from the scant attention granted to this ligating moiety in binding trivalent metal ions—despite its presence as a naturally occurring iron chelator in some classes

(12) TEXSAN/TEXRAY structure analysis package which includes versions of the following: DIRDIF, direct methods for different 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.

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

(14) The space group is polar, not chiral (both Δ and Λ isomers are generated by the two glide planes), hence the use of the term polarity as opposed to absolute configuration.

(15) Andreasch, R. *Monatsh. Chem.* **1884**, *5*, 33.

Table II. Selected Bond Lengths (Å) with Estimated Deviations in Parentheses for $M(oz)_3 \cdot CH_3OH$

distance	M = Al	M = Ga	M = In
M(1)–O(1)	1.844 (2)	1.934 (2)	2.103 (2)
M(1)–O(3)	1.877 (2)	1.981 (2)	2.149 (2)
M(1)–O(5)	1.838 (2)	1.929 (2)	2.104 (2)
M(1)–N(1)	2.042 (2)	2.075 (3)	2.233 (2)
M(1)–N(2)	2.004 (2)	2.040 (3)	2.208 (2)
M(1)–N(3)	2.001 (2)	2.028 (2)	2.199 (2)
O(1)–C(1)	1.313 (3)	1.315 (4)	1.312 (3)
C(1)–C(2)	1.405 (3)	1.406 (4)	1.410 (3)
C(2)–C(7)	1.447 (3)	1.443 (4)	1.450 (3)
C(7)–N(1)	1.292 (3)	1.295 (4)	1.291 (3)
C(7)–O(2)	1.343 (3)	1.349 (4)	1.350 (3)
O(2)–C(9)	1.451 (3)	1.456 (4)	1.446 (3)
C(9)–C(8)	1.511 (3)	1.524 (4)	1.511 (4)
C(8)–N(1)	1.473 (3)	1.477 (4)	1.472 (3)

Table III. Selected Bond Lengths (Å) with Estimated Deviations in Parentheses

distance	$Al(moz)_3$	$Ga(aloz)_3$	distance	$Al(moz)_3$	$Ga(aloz)_3$
M(1)–O(2)	1.847 (2)	1.920 (2)	C(4)–C(5)	1.413 (3)	1.418 (5)
M(1)–O(4)	1.849 (2)	1.938 (2)	C(3)–C(4)	1.446 (3)	1.448 (5)
M(1)–O(6)	1.847 (2)	1.923 (2)	C(3)–N(1)	1.281 (3)	1.282 (4)
M(1)–N(1)	1.988 (2)	2.027 (3)	C(3)–O(1)	1.341 (3)	1.346 (4)
M(1)–N(2)	2.021 (2)	2.061 (3)	O(1)–C(2)	1.460 (3)	1.442 (4)
M(1)–N(3)	2.044 (2)	2.038 (3)	C(2)–C(1)	1.519 (4)	1.514 (5)
O(2)–C(5)	1.313 (3)	1.310 (4)	C(1)–N(1)	1.471 (3)	1.471 (3)

Table IV. Selected Bond Angles (deg) with Estimated Deviations in Parentheses for $M(oz)_3 \cdot CH_3OH$

angle	M = Al	M = Ga	M = In
O(1)–M(1)–O(3)	173.80 (8)	174.28 (9)	165.67 (7)
O(1)–M(1)–O(5)	92.21 (8)	91.91 (9)	96.77 (7)
O(1)–M(1)–N(1)	87.31 (7)	87.88 (9)	83.72 (7)
O(5)–M(1)–N(1)	179.44 (8)	179.63 (9)	174.87 (7)
N(1)–M(1)–N(2)	91.79 (8)	92.5 (1)	96.39 (7)
N(1)–M(1)–N(3)	89.85 (7)	90.64 (9)	90.57 (7)
M(1)–O(1)–C(1)	135.6 (2)	132.4 (2)	132.9 (2)
M(1)–N(1)–C(7)	127.2 (2)	126.3 (2)	126.3 (2)
M(1)–N(1)–C(8)	125.9 (2)	125.2 (2)	124.9 (2)
C(7)–O(2)–C(9)	107.0 (2)	107.2 (2)	107.5 (2)
C(7)–N(1)–C(8)	106.9 (2)	108.4 (3)	108.8 (2)
C(1)–C(2)–C(7)	119.5 (2)	121.0 (3)	122.8 (2)
O(2)–C(7)–N(1)	117.0 (2)	116.0 (3)	115.2 (2)
N(1)–C(8)–C(9)	104.8 (2)	103.6 (3)	103.5 (2)
O(2)–C(9)–C(8)	104.3 (2)	104.8 (2)	104.9 (2)

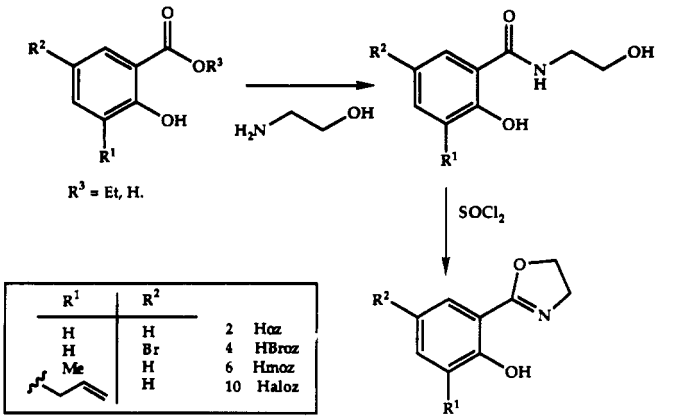
Table V. Selected Bond Angles (deg) with Estimated Deviations in Parentheses

angle	$Al(moz)_3$	$Ga(aloz)_3$
O(2)–M(1)–N(4)	97.02 (8)	175.80 (1)
O(2)–M(1)–O(6)	175.06 (9)	94.4 (1)
O(2)–M(1)–N(1)	88.54 (8)	87.7 (1)
O(6)–M(1)–N(2)	93.82 (9)	175.4 (1)
N(1)–M(1)–N(2)	174.95 (9)	90.5 (1)
N(1)–M(1)–N(3)	94.77 (8)	176.9 (1)
M(1)–O(2)–C(5)	133.8 (2)	129.6 (2)
M(1)–N(1)–C(3)	127.3 (2)	125.8 (2)
M(1)–N(1)–C(1)	124.1 (2)	125.8 (2)
C(2)–O(1)–C(3)	106.5 (2)	107.2 (3)
C(1)–N(1)–C(3)	108.1 (2)	108.3 (3)
C(3)–C(4)–C(5)	119.1 (2)	120.1 (3)
O(1)–C(3)–N(1)	116.7 (2)	115.9 (3)
N(1)–C(1)–C(2)	103.5 (2)	103.6 (3)
O(1)–C(2)–C(1)	104.1 (2)	104.6 (3)

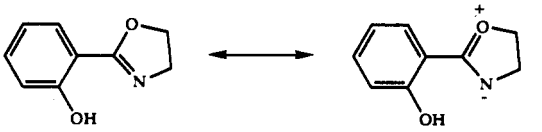
of siderophores. In planning for this undertaking, we adopted a retro biomimetic approach, and aimed first for the synthesis of the simplest examples of such systems, in order to investigate their coordination chemistry.

The synthesis of the 2-(2′-hydroxyphenyl)-2-oxazolines used in this study involved the condensation of 2-aminoethanol with a number of salicylic acid derivatives followed by dehydrative cyclization of the resulting β-hydroxyamide (Scheme I). As a

Scheme I



Scheme II



practical matter, the dehydrative cyclization of the intermediate β-hydroxyamide, although straightforward, showed some solvent dependency; e.g., compound **9**, when treated with thionyl chloride in CH_2Cl_2, failed to form an oxazoline, whereas the same reaction conducted in diethyl ether proceeded smoothly. A notable aspect of this synthetic scheme is that it lends itself readily toward substitution either on the aromatic ring, or on the oxazoline ring. This is a particularly desirable feature which can be exploited to vary the overall lipophilicity of the metal complex in order to achieve a certain degree of control over its mobilization in vivo.[1b,17]

The 2-(2′-hydroxyphenyl)-2-oxazolinates act as bidentate ligands via the phenolate oxygen and the oxazoline ring nitrogen. The *o*-hydroxy substituent plays a vitally important secondary role by imparting stability against hydrolysis to the oxazoline ring. To this end, in a low pH UV spectrophotometric study, Neilands and co-workers concluded that the unusual stability of the 2-(2′-substituted)-2-oxazolines is stereoelectronic in origin, i.e., due to a resonance contribution of hydroxyl (or alkoxy) oxygen nonbonding electrons with the π system, when the group is coplanar.[18]

X-ray diffraction studies of the oxazoline ring indicate double bond character in both C–O and C–N bonds as shown in Scheme II.[19] Given the charged nature of the second resonance structure, the oxazoline nitrogen would be expected to be a stronger hydrogen bond acceptor than the oxygen. This has two important consequences for the ligating ability of the 2-(2′-hydroxyphenyl)-2-oxazolines: first, it preorganizes the ligand via an intramolecular hydrogen bond between the hydroxyl substituent on the aromatic ring and the oxazoline nitrogen, thereby fixing the conformation of the appropriate rotamer; second, it increases the degree of hardness of the oxazoline nitrogen relative to an imine nitrogen, hence augmenting its ability to coordinate to hard acids such as the group 13 metal ions. Therefore, unlike Schiff base ligands, the favorable stereoelectronics of the 2-(2′-

(16) Meyers, A. I.; Mihelich, E. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 270. Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 567. Gant, T. G.; Meyers, A. I. *J. Am. Chem. Soc.* **1992**, *114*, 1010. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726. Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728. Suga, H.; Shi, X.; Fujieda, H.; Ibata, T. *Tetrahedron Lett.* **1991**, *47*, 6911. Müller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232.
(17) Zhang, Z.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1991**, *30*, 509.
(18) Peterson, T.; Falk, K.-E.; Leong, S. A.; Klein, M. P.; Neilands, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 7715.
(19) Also see: Eng-Wilmot, D. L.; van der Helm, D. *J. Am. Chem. Soc.* **1980**, *102*, 7719.

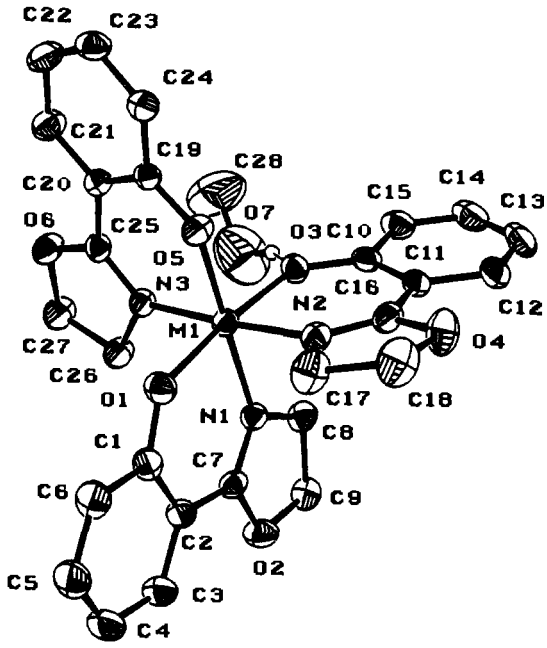


Figure 1. ORTEP view of the isostructural and isomorphous $M(oz)_3 \cdot CH_3OH$ (M = Al, Ga, In).

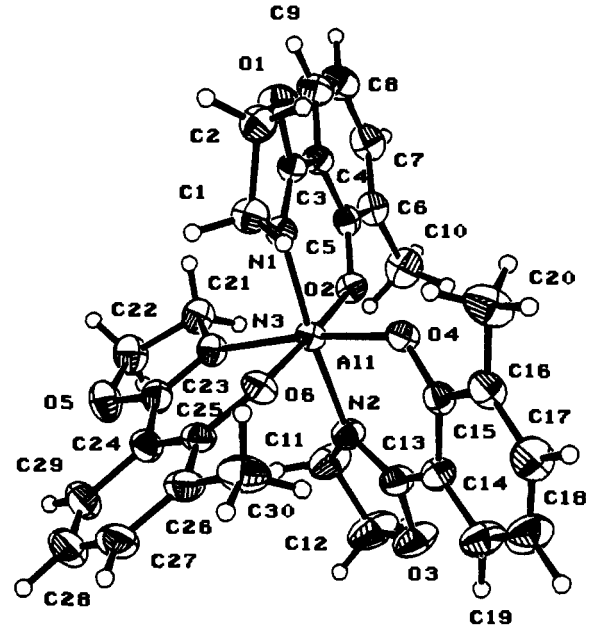


Figure 2. ORTEP view of $Al(moz)_3$.

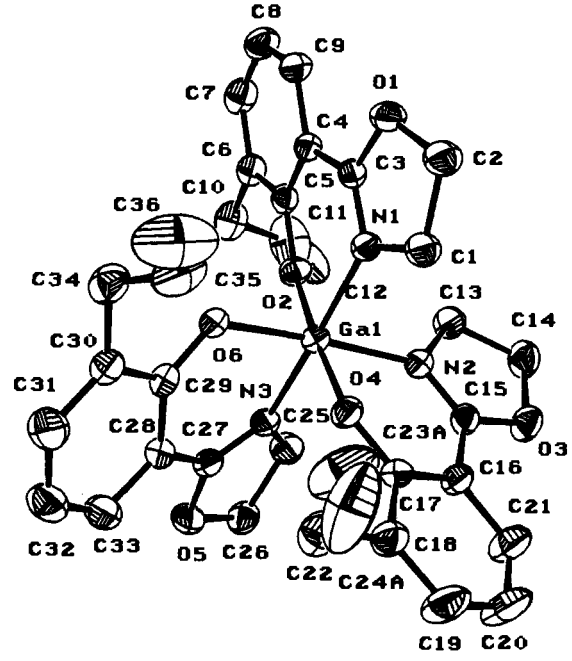


Figure 3. ORTEP view of $Ga(aloz)_3$. For clarity, only the predominant allyl group orientations are shown.

hydroxyphenyl)-2-oxazolines circumvents the problem of ligand hydrolysis[20] while providing a "harder" imine-type nitrogen donor. Clearly, these features are of paramount importance in designing ligands with great hydrolytic stability and high affinity for the group 13 metal ions, if the metal complexes are to be useful for in vivo studies.

Metal Complexes. The 12 metal complexes reported herein were prepared from methanol/water in the presence of slightly greater than 3 equiv of an aqueous base (1 M NaOH). All the complexes are quite lipophilic; they are very soluble in polar organic solvents, but only sparingly soluble (<1 mM) in water. Analyses for C, H, and N (and Br where appropriate) in each complex are consistent with the formulations of tris(ligand)metal species; notable exceptions are found in the $M(oz)_3$ series, which analyze (and crystallize) as methanol solvates (vide infra). Analytical results corresponding to solvent-free ML_3 formulations could not be found even by drying at ca. 50 °C in vacuo (<0.3 Torr) for 48 h.

The mass spectra of the complexes in EI mode show the expected ML_3^+, ML_2^+, ML^+, L^+ fragmentation, consistent with the formulation. In addition, the IR spectral pattern of the ligands is virtually preserved in the complexes with a general bathochromic shift (most conspicuously in case of $\nu_{C=N}$) upon complexation. The proton NMR data are also in accord with coordination of the metal ions by the ligands. The relatively complex spectra of Al and Ga complexes (see Experimental Section) is indicative of the fact that, in solution, these complexes exist as *mer* isomers. In the $M(oz)_3 \cdot CH_3OH$ complexes, coupling of the methanol CH_3 and OH protons, giving rise to a doublet and a quartet respectively, was observed despite the presence of relatively large amounts of dissolved water in the NMR solvent. Therefore, it can be concluded that these complexes are present as methanol adducts even in solution.

X-ray Crystallography. The crystal structures of $M(oz)_3 \cdot CH_3OH$ complexes (M = Al, Ga, In) (Figure 1) are all isomorphous and isostructural, except for the replacement of the metal atom. These complexes, as well as $Al(moz)_3$ (Figure 2) and $Ga(aloz)_3$ (Figure 3), all crystallize as *mer* isomers. There is a slight compression of the $In(oz)_3$ units perpendicular to the O(1)N(2)O(5) trigonal face leading to O(1)–In–N(1) angles of 84° (as compared to 87 and 88° for Al and Ga analogs, respectively). Similarly, in comparing the exocyclic N(1)–M–N(2) and O(1)–M–O(5) angles, the largest deviation was observed for In with corresponding angles of 96 and 97° respectively. Inspection of the chelate ring torsion angles in the three metal complexes reveals no significant deviation from planarity. An examination of the geometry around the metal centers in the $M(oz)_3$ series shows that the In complex is the most distorted from true octahedral geometry, whereas the Ga complex is the least distorted. By this criterion, Ga(III), which has a very similar ionic radius to Fe(III) (0.645 Å),[21] best fits the 2-(2′-hydroxyphenyl)-2-oxazolinate anion. This is not too surprising in light of the fact that nature has chosen this ligating moiety for Fe(III) sequestration. In every compound, M–O distances were shorter than M–N distances. Comparison of the metal-to-ligand bond lengths,

(20) Berg, D. J.; Rettig, S. J.; Orvig, C. *J. Am. Chem. Soc.* **1991**, *113*, 2528.

(21) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

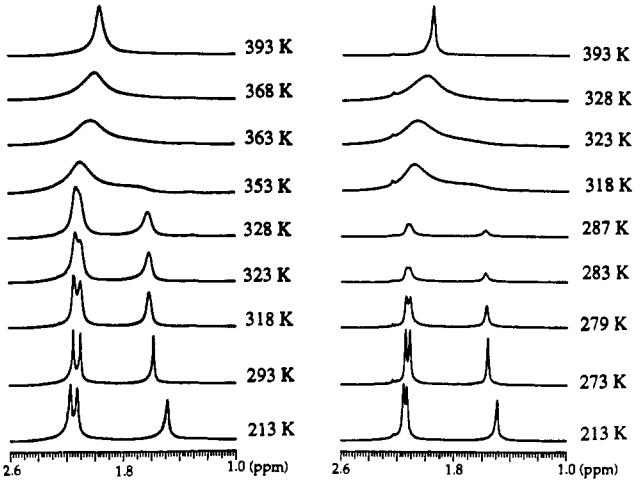


Figure 4. Variable-temperature ^{1}H NMR spectra (DMF-d_7) of the methyl region of Al(moz)$_3$ (left) and Ga(moz)$_3$ (right).

corrected for the difference in ionic radii of Al^{3+}, Ga^{3+}, and In^{3+}, reveals a relatively shorter M–N bond for Ga and In than for Al.[22]

The Al(moz)$_3$ structure exhibits a higher degree of distortion from ideal octahedral geometry as evinced from a comparison of the chelate ring bond angles with those of the more symmetric Al(oz)$_3$. Accordingly, each of the three chelate rings about the Al center in Al(moz)$_3$ show different degrees of deviation from planarity, the largest deviation being 0.1753 Å for the plane defined by Al(1)–O(4)–N(2)–C(13)–C(14)–C(15). Similarly, Ga(aloz)$_3$ is more distorted than Ga(oz)$_3$. In the solid state, Ga(aloz)$_3$ suffers a disorder only pertaining to the allyl substituents.

VT ^{1}H NMR Studies. Three unsymmetrical bidentate ligands situated around a central metal can give rise to two optical isomers (Δ and Λ)[24] and two geometric isomers (*fac* and *mer*).[25] In solution, geometric isomerization and racemization can occur, and such rearrangement reactions can be investigated by variable-temperature ^{1}H NMR spectroscopy. According to the Gordon and Holm classification,[25c] tris(ligand)metal complexes of group 13 metals are "fast", meaning that the rates of intramolecular rearrangements are fast enough to prevent resolution or separation of the isomers but not so rapid as to hinder isomer detection by NMR spectroscopy or other techniques such as low-temperature HPLC.[26] The M(moz)$_3$ complexes were chosen for study since the –CH_3 signals in these complexes are unencumbered by other proton signals in the molecule, thereby allowing the facile differentiation of geometrical isomers (and possibly the chiral nature of each in the slow exchange limit).[27] In addition, DMF-d_7 was deemed to be the ideal solvent for these experiments due to its excellent solvating ability and its large liquid temperature range.

The room-temperature spectra of Al(moz)$_3$ and Ga(moz)$_3$ (Figure 4) show three distinct –CH_3 singlets; no signals attributable to the corresponding *fac* isomers were detected. Furthermore, a comparison of the integration of the –CH_3 singlets and the oxazoline ring protons or the aromatic ring protons, confirms the assignment that the three singlets observed are *solely* due to the *mer* isomer in solution. Unless the complexes are sterically constrained, a statistical or nearly statistical distribution of isomers (i.e. four peaks with *fac* isomer accounting for 25% of total concentration) would usually be formed.[28] Therefore, the sterically hindered asymmetric bidentate moz$^-$ ligand is evidently capable of rigidly imposing a *mer* geometry about the Al and Ga centers at room temperature, to the total exclusion of the *fac* isomer. As expected, the low-temperature spectra of Al(moz)$_3$ and Ga(moz)$_3$ were not very revealing; racemization cannot be observed in this case because Δ-*mer* and Λ-*mer* constitute an enantiomeric pair. In contrast to the Al and Ga complexes, the room temperature spectrum of In(moz)$_3$ shows a single –CH_3 hydrogen signal. There is some broadening of this signal at –60 °C (see Figure 5) but not enough to suggest new sets of resonances. The room temperature spectrum of the In complex can be interpreted as resulting from the rapid rearrangement of the inequivalent ligand sites in *mer* geometry (vide infra).

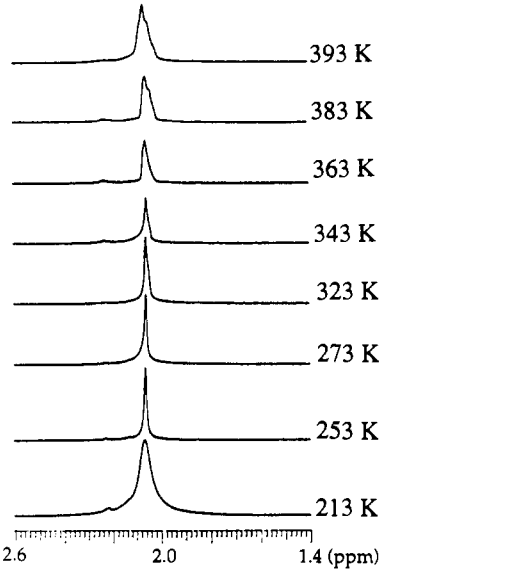


Figure 5. Variable-temperature ^{1}H NMR spectra (DMF-d_7) of the methyl region of In(moz)$_3$.

High-Temperature ^{1}H NMR Studies. When the temperature was raised (from ~20 to 120 °C), two dynamic interconversion processes were observed for the Al and Ga complexes (see Figure 4). These interconversion processes are interpretable as the environmental averaging (or ligand scrambling) of (a) the two most similar ligand sites of the *mer* isomer (the lower temperature process), and of (b) all three nonequivalent ligand sites of the *mer* isomer (the higher temperature process). The high-temperature ^{1}H NMR spectra of In(moz)$_3$ (Figure 5) show a singlet below ~90 °C, at which temperature a broadening of the signal gradually appears until a distinct shoulder is observed at 110 °C; this can be interpreted as the interconversion between the *mer* isomer and the thermodynamically less favorable *fac* isomer. This conclusion also corroborates the assignment of the high-temperature process observed in the Al and Ga complexes as a *mer* interconversion, since it is unlikely the *fac* isomer could account for the singlet –CH_3 hydrogen resonance at the coalescence temperature.

Evidence for the Intramolecular Nature of the Rearrangement Process. In order to obtain mechanistic information about the rearrangement reaction, it is necessary to ascertain whether or

(22) This observation is in accord with the order of absolute hardness[23] of Al^{3+} (η = 45.77), Ga^{3+} (η = 17), and In^{3+} (η = 13), hence the lesser affinity of Al^{3+} for (softer) N donors.
(23) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.
(24) York, R. J.; Bonds, W. D., Jr.; Costoradis, B. P.; Archer, R. D. *Inorg. Chem.* **1969**, *8*, 789.
(25) (a) Piper, T. S. *J. Am. Chem. Soc.* **1961**, *83*, 3908. (b) Fay, R. C.; Piper, T. S. *Inorg. Chem.* **1964**, *3*, 348. (c) Gordon, J. G., II; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5319. (d) Girgis, A. Y.; Fay, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 7061.
(26) Henderson, D. E.; Saltzmann, J. J.; Uden, P. C.; Cheng, Z. *Polyhedron* **1988**, *7*, 369.
(27) The *fac* isomer has a 3-fold symmetry axis but the *mer* is asymmetric. Therefore, the three ligand environments in the *fac* isomer are magnetically equivalent, and the chemical shifts of the nuclei on these ligands will be different from those of their inequivalent counterparts in the *mer* isomer.
(28) The *mer* isomer is both sterically (ligands are held farthest apart) and electronically (lower dipole moment) the thermodynamically more favorable isomer.[25c]

Table VI. ^{1}H NMR Coalescence Temperatures (T_c) and Calculated ΔG^* Values

compd	T_c, K	ionic radius, Å	ΔG^*, kcal/mol
$Al(moz)_3$	333 (±2)	0.535	17.3 (±0.3)
	366 (±2)		17.4 (±0.1)
$Ga(moz)_3$	287 (±2)	0.620	15.3 (±0.1)
	326 (±2)		15.4 (±0.1)
$In(moz)_3$	<213	0.800	<10[a]

[a] Estimated value based on the smallest chemical shift difference observed for the methyl signals least far apart in $Ga(moz)_3$ (at 253 K).

not the process is intramolecular. This can be accomplished by examining the ^{1}H NMR spectrum of a mixture of the tris(ligand)-metal complex of interest and another (similar) metal complex. If it takes an appreciable time to form the mixed ligand species, it can be concluded that ligand exchange is slower than the rearrangement reaction.[29] Equilibration of DMSO-d_6 solutions containing $M(moz)_3$ and $M(oz)_3$ results in the formation of mixed-ligand complexes $M(moz)_{3-n}(oz)_n$; however, the formation of the mixed ligand species is rather slow compared to the rate of intramolecular rearrangement. A 3:1 mixture of $Al(moz)_3$ and $Al(oz)_3$ contained no signals that could be attributed to mixed-ligand species after 30 min at room temperature; the equilibration appeared to be faster for the analogous Ga complexes as signals due to mixed species began to appear after 30 min at room temperature. Complete equilibration for both Al and Ga complexes was accomplished by heating the samples at ~100 °C for ca. 1 h. It can be concluded that the intermolecular process of ligand exchange occurs at a slower rate; the rearrangement reaction is, therefore, considered to be an *intra*molecular process.

The observed rates of interconversion of *mer* geometries are quantified by calculating an estimated value for the corresponding ΔG^* using Eyring's equation (Table VI).[31] The coalescence of the *three* inequivalent sites was treated as two separate exchange processes between two sites (which provided an estimate of ΔG^* for the corresponding two processes). To correct for the temperature dependence of the chemical shifts (which is presumably due to solvent–solute interactions[25b]), $\Delta\nu_e$ (the experimentally observed frequency separation) was plotted against temperature in the region of slow exchange.[33] The value of $\Delta\nu_c$ was read from the extrapolated line (linear least-square fit) at T_c. The margin of error was calculated for each value of ΔG^* using the correlation coefficient of the extrapolated line and the (±2K) uncertainty in the temperature measurements. Inspection of the results clearly reveals that the $M(moz)_3$ complexes exhibit the predicted kinetic order (Al < Ga < In).[34] The trend in ΔG^* (Al > Ga > In) is consistent with either bond rupture (five-coordinate transition state) or twist mechanisms (Bailar or Rây–Dutt twists) or both.[25b]

VT ^{27}Al NMR Studies. In order to further ascertain that the temperature dependent solution behavior observed is due to the interconversion of *mer* isomers, variable-temperature ^{27}Al NMR studies were undertaken. Despite the fact that Al, Ga, and In all possess magnetically active isotopes, Al has proved most amenable to direct observation by NMR because of a high intrinsic sensitivity and the existence of only one isotope.[35] ^{27}Al has an intrinsic sensitivity of 0.206 relative to ^{1}H, and a quadrupolar spin $^5/_2$ nucleus of 100% natural isotopic abundance. The nuclear quadrupole moment ($Q = 0.149 \times 10^{-24}$ cm^2) interacts with the electric field gradient (at the nucleus) that couples the nucleus with molecular motions; an efficient molecular relaxation mechanism ensues.[36] As a result, ^{27}Al line widths may vary from 3 Hz to several kilohertz, depending on a number of factors that affect the quadrupolar relaxation, most notably the symmetry about the metal center. However, other factors such as the rate of tumbling of the molecule, which is a function of both the size and the solvent viscosity (which is, in turn, temperature dependent), can also play a part in determining the line widths and, as such, need to be considered as well.

Table VII. ^{27}Al NMR Chemical Shifts and Line Widths at Various Temperatures in DMF-d_7

	T = 19.5 °C		T = 60 °C		T = 120 °C	
compd	δ, ppm	$W_{1/2}$, Hz	δ, ppm	$W_{1/2}$, Hz	δ, ppm	$W_{1/2}$, Hz
$Al(oz)_3$	6.9	840	7.2	560	7.6	280
$Al(Broz)_3$	7.4	1020	7.7	560	8.2	370
$Al(moz)_3$	8.5	930	8.2	560	8.4	370
$Al(aloz)_3$	8.3	840	8.0	560	8.5	370

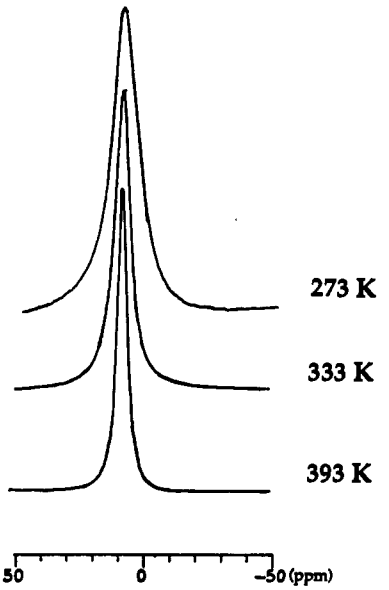


Figure 6. Variable-temperature ^{27}Al NMR spectra of $Al(moz)_3$ in DMF.

A significant narrowing (greater than 50%) of ^{27}Al line widths is observed as the temperature is raised from 20 °C to 120 °C for all four Al complexes in both DMSO (see Experimental Section) and DMF (Table VII and Figure 6). Although the absolute values of $W_{1/2}$ varied greatly depending on the NMR solvent used, the same trend, i.e. a greater than 50% narrowing of the ^{27}Al line widths, was observed in each solvent. Furthermore, in a control experiment, the variable-temperature ^{27}Al spectra of 0.1 M $Al(ClO_4)_3$ in DMF were obtained. The highly symmetric structure of $[Al(DMF)_6]^{3+}$ means that the ^{27}Al line width observed at room temperature is relatively narrow ($W_{1/2}$ = 93 Hz).[37] The line widths are found to be identical irrespective of the temperature at which the spectrum is obtained, clearly indicating that the narrowing of the line widths observed in the aforementioned Al complexes is not due to a solvent viscosity effect. A comparison of the line widths for $Al(oz)_3$ and $Al(aloz)_3$ further indicates that

(29) For example, no ^{1}H NMR signals attributable to mixed ligand species were detected in one hour at room temperature for a mixture of Al(acac)$_3$ and tris(1-phenyl-5-methylhexane-2,4-dionato)aluminum.[30]

(30) Hutchison, J. R.; Gordon, J. G., II; Holm, R. H. *Inorg. Chem.* **1971**, *10*, 1004.

(31) The Eyring equation (assuming a transmission coefficient of unity): $\Delta G^* = -RT_c \ln\{(\pi\Delta\nu_c h)/(k_B T_c 2^{1/2})\}$, where R = the gas constant, T_c = coalescence temperature; $\Delta\nu_c$ = the chemical shift separation in Hz at coalescence; h = the Planck constant; and k_B = the Boltzmann constant.[32]

(32) Thomas, W. A. *Annu. Rev. NMR Spectrosc.* **1968**, *1*, 43.

(33) For the lower temperature exchange the $\Delta\nu_e$ between two similar $-CH_3$ singlets was used; for the higher temperature exchange, $\Delta\nu_e$ was taken as the difference between the CH_3 signals which were farthest apart.

(34) The intramolecular lability of d^0 and d^{10} metals are dependent on the ionic radius of the metal. See for instance: Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Muetterties, E. L. *J. Am. Chem. Soc.* **1973**, *95*, 1116; Pignolet, L. H. *Top. Curr. Chem.* **1975**, *56*, 91.

(35) Delpuech, J. J. In *NMR of Newly Accessible Nuclei*; Lazlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 153–195.

(36) Akitt, J. W. *Prog. NMR Spectrosc.* **1989**, *21*, 1.

(37) Fratiello, A.; Kubo-Anderson, V.; Azimi, S.; Fowler, C.; Marinez, E.; Perrigan, R.; Shayegan, S.; Yao, B. *Magn. Reson. Chem.* **1992**, *30*, 280. Movius, W. G.; Matwiyoff, N. A. *Inorg. Chem.* **1967**, *6*, 847.

the changes observed do not correlate with the tumbling rate of the molecule (which is a function of size of the molecule). In fact, at 120 °C, the line widths of the Al complexes (except Al(oz)$_3$) are identical (370 Hz). The oz$^-$ anion is the most symmetric of the four bidentate ligands; hence, at the high-temperature limit, where fast interconversion of the *mer* isomers prevails, Al(oz)$_3$ exhibits the narrowest line width ($W_{1/2}$ = 280 Hz). At 120 °C, the line width of the ^{27}Al signal is determined by the ligand symmetry, whereas at an intermediate stage in the interconversion process (e.g. at ca. 60 °C) the line widths are under the kinetic control of the interconversion process, as reflected in the 560-Hz line width observed for all four Al complexes (Table VII).

Concluding Remarks. As a first step in studying the coordination chemistry of the biologically relevant 2-(2′-hydroxyphenyl)-2-oxazolinato ligating moiety with group 13 metal ions, the 12 metal complexes reported herein were synthesized and characterized. The X-ray crystallographic results revealed that such bidentate ligands can effect metal ligation via an {N,O} donor atom set to form pseudooctahedral complexes; all five structures were *mer*, and it was observed that Ga^{3+} (closest in size to Fe^{3+}) best fitted the geometrical constraints of the tris(ligand) coordination in an octahedral geometry. The solution studies (VT ^{1}H NMR and VT ^{27}Al NMR) indicated that the 2-(2′-hydroxyphenyl)-2-oxazolines are capable of rigidly enforcing the *mer* geometry about the metal center, almost to the exclusion of the less stable *fac* isomer in the −60 to +120 °C range. This can be best explained in terms of the sterically bulky nature of the complexes accentuating the stability of the *mer* (vis à vis *fac*) isomer. The ^{1}H NMR studies also revealed the *intra*molecular nature of the interconversion processes observed. Both twist and bond rupture mechanisms are in accord with the findings of this investigation thus far.

Measurement of the stability constants of these metal complexes is currently under investigation. In addition, we are vigorously pursuing the syntheses of the related multidentate ligands based on 2-(2′-hydroxyphenyl)-2-oxazoline and the analogous 2-(2′-hydroxyphenyl)-2-thiazoline systems.[38] The results will be reported in due course.

Acknowledgment is made to the NSERC of Canada and the U.S. Public Health Service (CA 48964) for operating grants. We are particularly indebted to Prof. James Trotter for the very kind use of his crystallographic facilities. We would also like to thank one of the reviewers for particularly insightful comments.

Supplementary Material Available: Complete tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, bond distances, bond angles, hydrogen atom coordinates, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-square planes for each of the five structures (134 pages). Ordering information is given on any current masthead page.

(38) Hoveyda, H. R.; Karunaratne, V.; Orvig, C. *Tetrahedron* **1992**, *48*, 5219.