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Article

Transition-Metal Complexes of a Bifunctional Tetradentate Gallium Alkoxide Ligand

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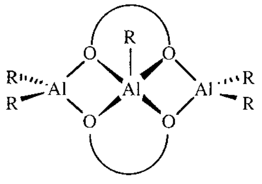
The mixed gallium transition-metal complexes $[FeCl\{Ga_2(^tBu)_4(neol)_2\}]$ (**1**) and $[M\{Ga_2(^tBu)_4(neol)_2\}]$, M = Co (**2**), Ni (**3**), Cu (**4**), have been prepared by the reaction of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ (neol-H_2 = 2,2-dimethyl-propane-1,3-diol) with the appropriate metal halide and Proton Sponge. Compounds **1**–**4** have been characterized by NMR (**3**), UV/vis, and IR spectroscopy and magnetic susceptibility (solution and solid state), and their molecular structures have been confirmed by X-ray crystallography. The molecular structure of compounds **1**–**4** consists of a tetracyclic core formed from two four-membered and two six-membered rings. The central metal atom adopts a square pyramidal (**1**) or square planar (**2**–**4**) geometry. The magnetic susceptibilities for **1**, **2**, and **4** are as expected for strong ligand field environments. On the basis of spectroscopic and structural data, the $[Ga_2(^tBu)_4(neol)_2]^{2-}$ ligand appears to be more flexible than other chelating ligands; this is proposed to be due to the flexibility in the O–Ga–O bond angle.

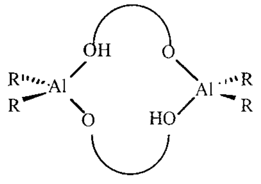
Introduction

In recent years there have been an increasing number of aluminum compounds that may be categorized as "linear" trimers (**I**), in which the terminal aluminum centers are four-coordinate and the central aluminum is five-coordinate. The simplest examples of this latter group are the pentaalkyltrialuminum compounds formed from the reaction of AlR_3 with aliphatic diols (**I**).[2–4] A number of related compounds have been reported with the salen class of N_2O_2 tetradentate ligands.[5] An alternate view of these compounds is of a five-coordinate aluminum complex of a bifunctional tetradentate ligand with an aluminum-containing backbone (**II**).

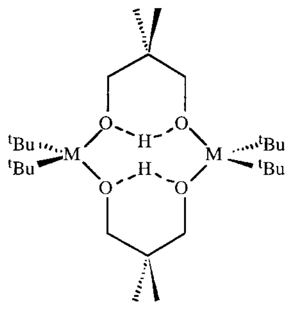
We have recently reported the reaction of $M(^tBu)_3$ (M = Al, Ga) with 2,2-dimethylpropane-1,3-diol (neol-H_2), which yields $[M_2(^tBu)_4(neol\text{-}H)_2]$ (**III**), and have demonstrated their application as bifunctional (two OH groups) tetradentate (4*O*) ligands toward aluminum and gallium fragments (**IV**).[6]



(**I**)

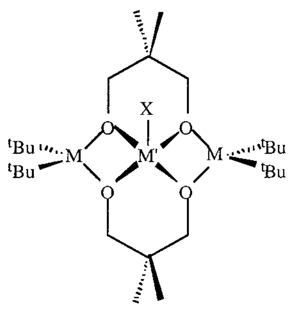


(**II**)



M = Al, Ga

(**III**)



M = Al, Ga, M' = Al, Ga, X = H, Me, ᵗBu, Cl

(**IV**)

Given the ligating ability of $[M_2(^tBu)_4(neol\text{-}H)_2]$ toward group 13 metals, a natural extension of these initial results is to investigate the reactivity with transition metals. Of particular interest are the late-first-row metals (i.e., Fe, Co, Ni, and Cu), due to their ability to form square planar complexes.

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10.1021/ic0106773 CCC: $22.00

Experimental Section

IR samples were prepared as Nujol mulls between KBr plates, unless otherwise stated. NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported relative to internal solvent resonances. Magnetic moments were measured using a Johnson Matthey MSB-1 Evans magnetic susceptibility balance[7] and by use of the Evans solution NMR method using a Bruker Avance 200 MHz spectrometer.[8] The UV absorption measurements were carried out using a Cary 910 UV/vis spectrophotometer. $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ was prepared according to literature procedures.[6] Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. All other chemicals were obtained from Aldrich and used without further purification (unless otherwise noted).

$[FeCl\{Ga_2(^tBu)_4(neol)_2\}]$ (1). A solution of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ (0.500 g, 0.874 mmol) and Proton Sponge (0.373 g, 1.74 mmol) in THF (100 mL) was brought to reflux, and then a solution of $FeCl_3$ (0.141 g, 0.874 mmol) in THF (20 mL) was added quickly over a period of 1 min. The reaction was refluxed for 6 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure. The resulting yellow-brown solid was extracted with pentane (3 × 50 mL). The extract was concentrated and cooled to −33 °C, resulting in the formation of brown blocks. Yield: 50%.

$[Co\{Ga_2(^tBu)_4(neol)_2\}]$ (2). A solution of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ (0.500 g, 0.874 mmol) and Proton Sponge (0.373 g, 1.74 mmol) in THF (100 mL) was brought to reflux, and then a solution of $CoCl_2$ (0.113 g, 0.874 mmol) in THF (20 mL) was added quickly over a period of 1 min. The reaction was refluxed for 6 h and allowed to cool to room temperature. The solvent was removed under reduced pressure. The resulting blue-green solid was extracted with pentane (3 × 50 mL). The extract was concentrated and cooled to −33 °C, resulting in the formation of blue-green crystals. Yield: 25%.

$[Ni\{Ga_2(^tBu)_4(neol)_2\}]$ (3). A solution of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ (0.500 g, 0.874 mmol) and Proton Sponge (0.373 g, 1.74 mmol) in toluene (100 mL) was brought to reflux. To this was added, over a period of 10 min, a solution of $(Ph_3P)_2NiCl_2$ (0.57 g, 0.874 mmol) in toluene (100 mL). The reaction was refluxed for 3 h and cooled to room temperature. The solution was concentrated and allowed to cool to −33 °C, whereupon a white precipitate (PPh_3) was observed. The reaction mixture was filtered, and the solution was concentrated and cooled to −33 °C. The resulting purple-pink crystalline material was isolated by filtration. Yield: 20%. ^1H NMR: δ 3.47 (8H, s, OCH_2), 1.48 [36H, s, $C(CH_3)_3$], [12H, s, $C(CH_3)_2$]. ^{13}C NMR: δ 73.4 (OCH_2), 35.2 [$C(CH_3)_2$], 31.4 [$C(CH_3)_3$], 22.4 [$C(CH_3)_2$].

$[Cu\{Ga_2(^tBu)_4(neol)_2\}]$ (4). A solution of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ (0.500 g, 0.874 mmol) and Proton Sponge (0.373 g, 1.74 mmol) in THF (100 mL) was brought to reflux, and a solution of $CuCl_2$ (0.117 g, 0.874 mmol) in THF (20 mL) was added quickly over a period of 1 min. The reaction was refluxed for 6 h, after which the solvent was removed under vacuum. The resulting bright purple material was extracted with pentane (3 × 50 mL). The extract was concentrated and cooled to −33 °C, resulting in the formation of dark purple crystals that were hand separated from the clear colorless crystals of $[Ga_3(^tBu)_5(neol)_2]$. Yield: 20%.

Crystallographic Studies. Crystals were sealed in glass capillaries under argon. Data were collected at ambient temperature on a Bruker CCD SMART system, equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å), and corrected for Lorentz and polarization effects. Data collection and cell determinations were performed in a manner previously described.[9] The structures were solved using the direct methods program XS[10] and difference Fourier maps and refined by using the full-matrix least-squares method.[11] As was observed for aluminum and gallium complexes of $[Ga_2(^tBu)_4(neol)_2]^{2-}$ and $[Al_2(^tBu)_4(neol)_2]^{2-}$,[6] at least one *tert*-butyl group exhibited dynamic disorder in a ratio of 1:1. The thermal parameters for the Ni in compound **3** are high; attempts to resolve the atom as partial occupancy could not be done sensibly. The poor diffraction of the crystals of **3** and the large thermal motion undoubtedly contribute to the high thermal motion of Ni(1). All non-hydrogen atoms (except the carbon atoms associated with the disordered *tert*-butyl group in compound **3**) were refined with anisotropic thermal parameters. All the hydrogen atoms were placed in calculated positions [$U_{iso} = 0.08$; $d(C-H) = 0.96$ Å] for refinement. Refinement of positional and anisotropic thermal parameters led to convergence (see Table 1).

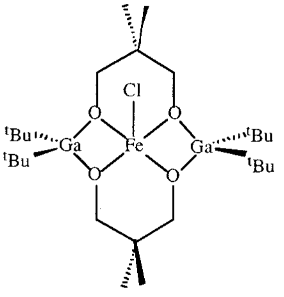
Table 1. Summary of X-ray Diffraction Data

	1	**2**	**3**	**4**
empirical formula	$C_{26}H_{56}FeClGa_2O_4$	$C_{26}H_{56}CoGa_2O_4$	$C_{26}H_{56}NiGa_2O$	$C_{26}H_{54}CuGa_2O_4$
M_w	637.43	605.06	604.82	609.67
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a, Å	11.022(2)	10.889(2)	9.262(2)	10.868(2)
b, Å	15.053(3)	11.073(2)	6.697(2)	11.091(4)
c, Å	20.814(4)	21.950(4)	10.776(2)	21.998(4)
α, deg		80.19(3)	65.90(3)	79.95(3)
β, deg	98.54(3)	81.19(3)	80.33(3)	80.92(3)
γ, deg		76.36(3)	69.63(3)	76.28(3)
V, Å^3	3415(1)	2516.6(9)	827.8(3)	2517.6(3)
Z	4	3	1	3
D_{calcd}, g cm^{-3}	1.290	1.249	1.265	1.258
μ_{calcd}, mm^{-1}	2.09	2.11	2.20	2.25
R[a]	0.0390	0.0609	0.1133	0.0473
R_w[a]	0.0960	0.1477	0.3151	0.1117

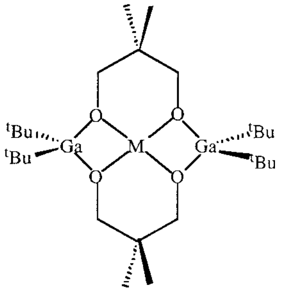
[a] $R = \sigma|F_o - F_c|/\sigma F_o$; $R_w = \{\sigma[\{w(F_o^2 - F_c^2)^2\}/\{w(F_o^2)^2\}]\}^{1/2}$.

Results and Discussion

The mixed gallium transition-metal complexes $[FeCl\{Ga_2(^tBu)_4(neol)_2\}]$ (**1**) and $[M\{Ga_2(^tBu)_4(neol)_2\}]$, M = Co (**2**), Ni (**3**), Cu (**4**), were prepared in modest yield by the reaction of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ with the appropriate metal halide and Proton Sponge; see the Experimental Section. The other major product observed was $[Ga_3(^tBu)_5(neol)_2]$, whose



(**1**)



M = Co (**2**), Ni (**3**), Cu (**4**)

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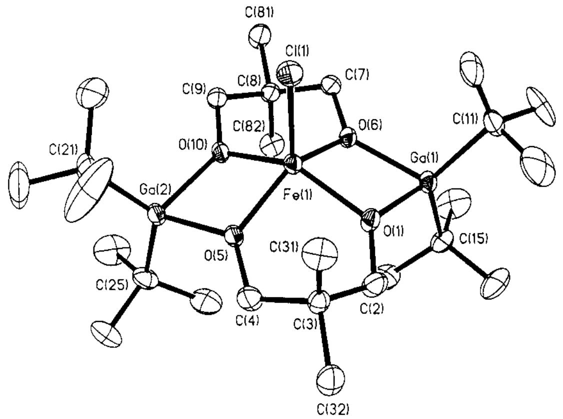

Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at the 20% level, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Fe(1)−O(1)	1.944(2)	Fe(1)−O(6)	1.944(2)
Fe(1)−O(10)	1.946(2)	Fe(1)−O(5)	1.945(2)
Fe(1)−Cl(1)	2.21(1)	Ga(1)−O(1)	1.972(2)
Ga(1)−O(6)	1.964(2)	Ga(1)−C(11)	1.986(4)
Ga(1)−C(15)	1.982(4)	Ga(2)−O(5)	1.974(2)
Ga(2)−O(10)	1.961(2)	Ga(2)−C(21)	1.986(4)
Ga(2)−C(25)	1.982(4)		
O(1)−Fe(1)−O(6)	78.6(1)	O(6)−Fe(1)−O(10)	89.7(1)
O(10)−Fe(1)−O(5)	78.1(1)	O(5)−Fe(1)−O(1)	91.1(1)
O(1)−Fe(1)−Cl(1)	111.47(8)	O(5)−Fe(1)−Cl(1)	111.74(8)
O(6)−Fe(1)−Cl(1)	104.28(8)	O(10)−Fe(1)−Cl(1)	104.76(8)
O(1)−Ga(1)−O(6)	77.4(1)	C(11)−Ga(1)−C(15)	126.6(2)
O(1)−Ga(1)−C(15)	109.3(2)	O(6)−Ga(1)−C(15)	109.3(1)
O(10)−Ga(2)−O(5)	77.0(1)	C(21)−Ga(2)−C(25)	128.3(2)
O(5)−Ga(1)−C(25)	110.3(2)	O(10)−Ga(1)−C(15)	110.7(2)

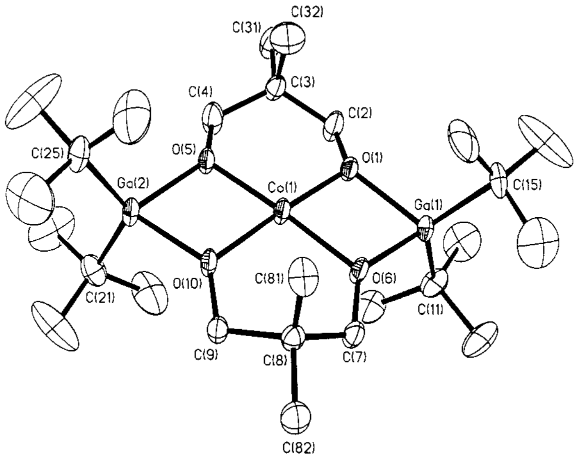

Figure 2. Molecular structure of **2**. Thermal ellipsoids are shown at the 20% level, and hydrogen atoms are omitted for clarity.

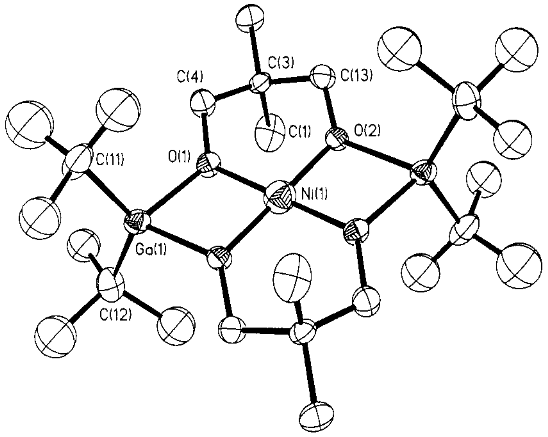

Figure 3. Molecular structure of **3**. Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

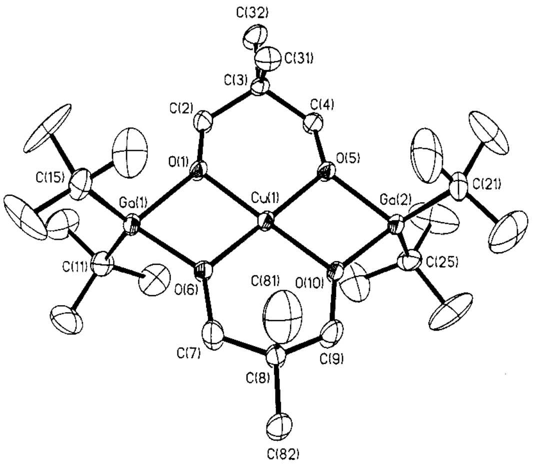

Figure 4. Molecular structure of one of the crystallographically independent molecules of **4**. Thermal ellipsoids are shown at the 20% level, and hydrogen atoms are omitted for clarity.

formation is due to a competitive side reaction of [Ga$_2$(^{t}Bu)$_4$(neol-H)$_2$] with Proton Sponge.[6] Compounds **1**−**4** have been characterized by NMR (**3**), UV/vis, and IR spectroscopy and magnetic susceptibility (solution and solid state), and their molecular structures have been confirmed by X-ray crystallography.

The molecular structure of **1** is shown in Figure 1; selected bond lengths and angles are given in Table 2. The structure consists of a tetracyclic core formed from two four-membered and two six-membered rings. The central iron atom adopts a square pyramidal geometry, in which four oxygen atoms occupy the basal sites in a manner similar to that of salen-type complexes.[12] The central iron atom is displaced 0.605 Å above the O$_4$ plane, while the gallium atoms are 0.385 Å below the plane. In comparison to [MX{Ga$_2$(^{t}Bu)$_4$(neol)$_2$}] (M = Al, Ga), the Fe−O distances are within the range expected from a comparison of the ionic radii of Fe^{3+} versus Al^{3+} and Ga^{3+}, and are within the range observed for salen-type ligands.[4] The six-membered M−O−C−C−C−O rings adopt a chair conformation, with the methyl groups on the quaternary carbons adopting axial and equatorial positions. The *tert*-butyl group associated with C(11) exhibits rotational disorder in a manner previously observed.[6]

The molecular structures of **2**−**4** are shown in Figures 2−4, respectively; selected bond lengths and angles are given in Table 3. Each structure consists of a tetracyclic core formed from two four-membered and two six-membered rings. The central transition-metal atom adopts a square planar geometry with the four oxygen donor atoms. The six-membered M−O−C−C−C−O rings adopt a chair conformation, with the methyl groups on the quaternary carbons adopting axial and equatorial positions. However, the relative

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(12) See, Shyu, H.; Wei, H.; Lee, G.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **2000**, 915 and references therein.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[M\{Ga_2(^tBu)_4(neol)_2\}]$

compd	M	M−O	Ga−O	Ga−C	O−M−O$_{cis}$	O−M−O$_{trans}$	C−Ga−C	O−Ga−O
2	Co	1.907(4)	1.949(3)	1.984(7)	98.5(2)	175.4(2)	129.2(3)	80.1(2)
		1.922(3)	1.939(4)	1.977(7)	98.2(2)	175.0(2)	129.4(3)	80.3(2)
		1.923(3)	1.933(3)	2.007(7)	81.4(2)			
		1.913(4)	1.944(3)	1.976(7)	80.3(2)			
3	Ni	1.795(9)	1.924(9)	1.96(2)	92.0(4)	179(1)	88.0(4)	80.8(4)
		1.807(9)	1.937(9)	1.97(2)	88.0(4)			
4	Cu	1.889(3)	1.931(4)	1.972(7)	98.9(2)	179.6(2)	128.0(3)	78.7(2)
		1.882(4)	1.926(4)	1.975(7)	98.3(2)	179.2(2)	128.4(3)	81.3(2)
		1.877(4)	1.942(4)	1.974(7)	78.7(2)			
		1.896(4)	1.939(4)	1.980(4)	81.3(2)			

Table 4. Comparison of M−O Bond Distances (Å) for Selected Square Planar Complexes

M	$[M\{Ga_2(^tBu)_4(neol)_2\}]$	M(β-diketonate)$_2$[a]	M(salen)[a]
Co	1.907(4)−1.923(3)	1.917(5)−1.922(4)	1.823(3)−1.853(4)
Ni	1.795(9)−1.807(9)	1.819(5)−1.847(4)	1.840(4)−1.903(5)
Cu	1.877(4)−1.896(4)	1.888(5)−1.929(4)	1.864(4)−1.907(5)

[a] Values for M(β-diketonate)$_2$ and M(salen) taken from the Cambridge Crystallographic Database with ESDs of C−C bonds <0.005 Å.

Table 5. Magnetic Moments μ_{eff} (μ_B), Electron Configuration, and UV Spectrum λ_{max} for $[FeCl\{Ga_2(^tBu)_4(neol)_2\}]$ and $[M\{Ga_2(^tBu)_4(neol)_2\}]$

complex	M	solid (298 K)	THF soln (298 K)	d^n	spin state	λ_{max} (nm)	e (L mol^{-1} cm^{-1})
1	Fe(III)	5.40	5.36	d^5	high spin	406	235
2	Co(II)	1.92	2.13	d^7	low spin	476	127
						617	156
3	Ni(II)	0.13	0.16	d^8	low spin	538	99
						626	115
4	Cu(II)	1.83	1.87	d^9	low spin	506	90
						594	130

conformation appears to be flexible since both syn and anti geometries are found.

The structure of **3** is centrosymmetric and similar to one of the two crystallographically independent molecules [Co(1A)] and [Cu(1A)] in **2** and **4**, respectively. As a consequence of the anti geometry, the quaternary carbons of the neol rings adopt a centrosymmetric structure. In contrast, the quaternary carbons of the neol rings in the molecules associated with Co(1) and Cu(1) adopt a syn geometry. This difference in conformation is also reflected by the displacement of the gallium atoms from the O_4 plane. Of the two crystallographically independent molecules of $[M\{Ga_2(^tBu)_4(neol)_2\}]$, the Ga atoms are displaced slightly above the O_4 plane (0.157 and 0.201 Å) in the noncentrosymmetric molecules, but not at all in the centrosymmetric molecules. The shortest nonbonded distances to the central transition metal involve axial methyl groups of the neol ligand [$M\cdots C_{methyl} = 3.463$ Å (Co), 3.348 Å (Ni), 3.50 Å (Cu)]. For compounds **2**−**4**, the *tert*-butyl groups associated with C(15) exhibit rotational disorder in a manner previously observed.[6]

It is worth comparing the M−O distances in compounds **2**−**4** with those in related complexes. Table 4 compares the M−O distances in $[M\{Ga_2(^tBu)_4(neol)_2\}]$ with those in M(β-diketonate)$_2$ and M(salen) complexes. The M−O distances for $[M\{Ga_2(^tBu)_4(neol)_2\}]$ (M = Ni, Cu) are slightly shorter than those in the M(β-diketonate)$_2$ and M(salen) analogues, whereas the Co−O bond lengths are about the same as those in the M(β-diketonate)$_2$ and smaller than those in the M(salen) complexes. In both the $[M\{Ga_2(^tBu)_4(neol)_2\}]$ and M(β-diketonate)$_2$ complexes the M−O bond lengths show a direct correlation to the ionic radii of the metal, indicating that $[Ga_2(^tBu)_4(neol)_2]^{2-}$ is a flexible ligand. This is in contrast to M(salen) complexes where the rigid geometry of the ligand commonly causes distortion from planarity and a lengthening of the M−O distances.[13] The lack of rigidity of the $[Ga_2(^tBu)_4(neol)_2]^{2-}$ ligand may be attributed to the flexibility in the O−Ga−O bond angle. This may be illustrated by comparing the O−Ga−O bond in the free ligand [89.6(1)°][6] to that in the metalated complex [78.7(2)−81.3(2)°], which indicates that the ligand alters its geometry to suit the coordination sphere of the metal. This flexibility may not be observed in normal hydrocarbon-based chelating complexes due to the prohibitive strain energy for carbon in a similar geometry.

Magnetic Susceptibility. Magnetic moments for compounds **1**−**4** have been calculated from measured magnetic susceptibilities in both the solid state and a THF solution by the Evans solid[7] and NMR[8] methods. Calculated values are given in Table 5.

The nickel(II) complex **3** is essentially diamagnetic, which is indicative of a low-spin d^8 square planar configuration and is consistent with other known Ni(II) chelated complexes.[14] The small amount of paramagnetism in compound **3** can be attributed to a number of sources, such as temperature-independent contributions[15] or weak temperature-dependent paramagnetism.[16] We have not investigated this effect at this time.

The magnetic moment for **1** of 5.40 μ_B (solid state) and 5.36 μ_B (solution) is indicative of a high-spin d^5 electron configuration, which is consistent with other tetradentate chelate complexes of five-coordinate iron(III), in particular those with strong ligand fields such as porphyrins and Schiff bases.[17] The calculated magnetic moments for the copper(II) and cobalt(II) complexes indicate these d^9 and d^7 ions have the expected $S = 1/2$ electron configuration. The magnetic moment found for **2** confirms the presence of a square planar geometry in both the solid state and solution.[18,19]

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Table 6. Selected λ_{max} Values, Cu−X Bond Lengths (Å), and X−Cu−X_{cis} Angles (deg) for Square Planar Chelate Cu(II) Complexes

ligand	structure type	λ_{max} (nm)	Cu−X (Å)	X−Cu−X_{cis} (deg)
$[Ga_2(^tBu)_4(neol)_2]_2$	**VII**	594	1.877(4)−1.896(4)	81.3(2)−98.9(2)
salicyaldehyde-diimine	**VI**	560−638	1.897(3)−1.915(9)	79.7(3)−95.9(3)
acetylacetone-diimine	**VI**	540−632	1.900(8)−1.940(8)	85.4(1)−100.1(1)
β-diketonate	**V**	650−680	1.912(4)−1.958(4)	86.8(2)−93.2(2)
oxalate	**V**	689	2.046	80.6−99.4
azamacrocycles	**VI**	594	2.01(3)−2.03(5)	85.7(2)−94.3(2)
diamine	**V**	654	2.01(1)−2.20(1)	87.21(9)−92.79(9)

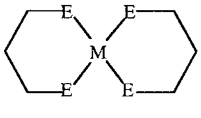
Electronic Spectra. The electronic spectra for $[FeCl\{Ga_2(^tBu)_4(neol)_2\}]$ and the $[M\{Ga_2(^tBu)_4(neol)_2\}]$ complexes have been determined in hexane solution. Compound **1** shows a single UV absorption, whereas the Co(II), Ni(II), and Cu(II) complexes **2**−**4** show the presence of two UV absorption bands (Table 5). These bands are undoubtedly due to metal d−d transitions, judging from their positions and intensities. The positions and intensities for complexes **2**−**4** correlate well with those of other square planar chelate complexes.[20]

3 absorbs at 538 and 626 nm with extinction coefficients of 99 and 115 L mol^{-1} cm^{-1} indicative of spin-allowed and Laporte forbidden transitions. These transitions correspond to excitation from the ground state ($^1A_{1g}$) to the excited states ($^1A_{2g}$ and $^1B_{1g}$). Similar results may be seen for **2**, with transitions from the ground state ($^2B_{2g}$) to the excited states ($^2B_{2g}$ and $^2A_{1g}$) at 476 and 617 nm. Due to the fact that there is only one transition observed in the UV spectrum of $[FeCl\{Ga_2(^tBu)_4(neol)_2\}]$, direct correlation to specific transitions is impossible, but is tentatively assigned to the single electron transition from the $d_{z^2}$to the $d_{x^2-y^2}$ orbital. For UV absorption of Cu(II) complexes such as **4**, there are two d−d absorption bands that may be unequivocally assigned to involve transitions from the d_{xy} and d_{z^2} orbitals to the $d_{x^2-y^2}$ orbital. This would indicate that 10 Dq for this complex is 594 nm.

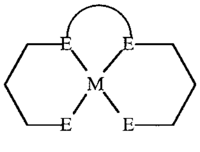
Although the 10 Dq values determined for the square planar complexes **2**−**4** are indicative of the strength of the ligand field, they do not provide a qualitative indication of the ligand field strength in relation to other metal chelate complexes. In this regard, we have attempted to compare the UV absorption of **4** with that of other Cu(II) chelates. The Cu(II) complex was chosen because a large number of square planar chelate complexes are stable and because the UV spectra are quite well understood. Table 6 shows the UV spectra λ_{max} values, bond lengths (Å), and bond angles (deg) for a series of Cu(II) N_2O_2 (salicylaldehydediimine[21] and acetylacetonediimine[22]), O_4 (acetylacetonate[23] and oxalate[24]), and N_4 (azamacrocycles[25] and diamine chelates[26]) chelating ligands.

The λ_{max} of 594 nm for **4** is an intermediate value of all the compounds listed in Table 6, which range from 540 to 689 nm. Comparison of **4** with chelate complexes with oxygen donors such as β-diketonates and oxalate shows that the $[Ga_2(^tBu)_4(neol)_2]^{2-}$ ligand imparts a stronger ligand field than traditional O_4 oxygen donors.

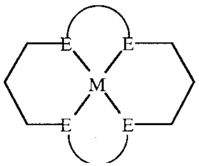
It is reasonable to expect that the increase in the observed ligand field is due to the increased flexibility of the chelating ligand, allowing closer interaction between the metal and the chelating ligand, and/or the increased bridging within the series M(β-diketonate)$_2$ (**V**) < M(salen) (**VI**) < $[M\{Ga_2(^tBu)_4(neol)_2\}]$ (**VII**).



(**V**)



(**VI**)



(**VII**)

In structure **V**, the ligands freely vibrate and twist about the metal. Placing a third bridging unit as shown in structure **VI** results in a loss of the vibrational freedom and more importantly dampens the out-of-plane twisting vibrations. Addition of a fourth bridging unit further decreases the vibrational freedom and severely restricts all out-of-plane twisting. As the vibrational and out-of-plane twisting in these complexes is reduced, the total interaction between the metal and the chelate donor atoms increases, thus producing a strong ligand field.

It is interesting to note that, irrespective of the identity of the donor ligand (O versus N), the λ_{max} for square planar Cu complexes with structures of type **V** are in the range 650−690 nm, while those for structure **VI** are in the range 540−640. This trend is in agreement with the increased constraints of the ligands. Compounds of type **VII** are within the range for those of type **VI**. This would suggest that the fourth bridging unit further does not significantly decrease the vibrational freedom of the complex.

Conclusions

The gallium alkoxide compound $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ has been shown to act as a bifunctional (two OH groups) tetradentate (4*O*) ligand toward late-first-row transition metals. From analysis of the crystal structures of these complexes, the $[Ga_2(^tBu)_4(neol)_2]^{2-}$ ligand is not rigid like many hydrocarbon-based chelates, but rather flexible. In

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addition, the electronic and magnetic properties of these complexes show that the $[Ga_2(^tBu)_4(neol)_2]^{2-}$ ligand forms a relatively strong ligand field for a 4*O* ligand geometry. The chemistry of the $[Ga_2(^tBu)_4(neol)_2]^{2-}$ ligand is under further investigation.

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Supporting Information Available: Full listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters and crystallographic data in CIF format. This material is available via the Internet at http://pubs.acs.org.

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