

Syntheses and Structures of Isoindoline Complexes of Zn(II) and Cu(II): An Unexpected Trinuclear Zn(II) Complex

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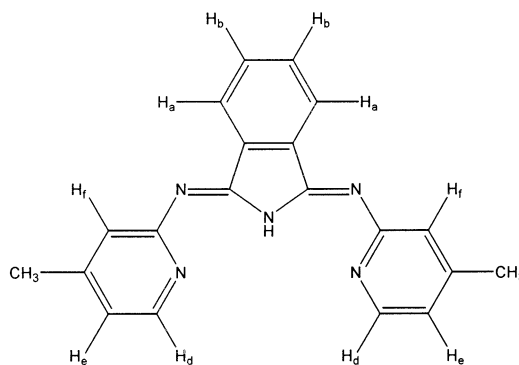
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Deprotonation of the tridentate isoindoline ligand 1,3-bis{2-(4-methylpyridyl)imino}-isoindoline, 4'-MeLH, and reaction with hydrated zinc(II) perchlorate produces an unexpected trinuclear Zn(II) complex, $[Zn_3(4'-MeL)_4](ClO_4)_2 \cdot 5H_2O$ (**1**), whereas reaction with hydrated copper(II) perchlorate in methanol produces the expected mononuclear product, $[Cu(4'-MeL)(H_2O)_2]ClO_4$ (**2**). X-ray diffraction shows that the trinuclear Zn(II) complex (**1**) contains a linear zinc backbone, and the arrangement of ligands about the outer chiral zinc(II) atoms is helical. The two terminal zinc ions exhibit approximate C_2 site symmetry, with tetrahedral coordination by two pyrrole and two pyridyl nitrogen atoms of the potentially tridentate isoindoline ligands. The central zinc ion exhibits approximate tetrahedral symmetry, with coordination by four pyridyl nitrogen atoms of four different isoindoline ligands. Pyridyl–pyrrole intramolecular π -stacking interactions contribute to the stability of the trinuclear cation. The structure of the mononuclear copper(II) complex cation in **2** is best described as a distorted trigonal bipyramid. The isoindoline anion binds Cu(II) in both axial positions and one of the equatorial positions; water molecules occupy the other two equatorial positions.

Introduction

Tridentate nitrogen donor ligands such as tris-pyrazolylborates¹ and triazacyclanones² have played an important role in inorganic chemistry in recent years, both as templates for models of metalloproteins and as templates for catalysis. We are interested in another class of tridentate nitrogen donors, the pincer-like isoindolines. The isoindoline ligand used in this study, 1,3-bis{2-(4-methylpyridyl)imino}isoindoline (hereafter 4'-MeLH), is shown below.

Isoindolines, which have been relatively unexplored and unexploited as chelating ligands, offer interesting possibilities for bidentate or tridentate coordination as a deprotonated anionic ligand. In contrast to the tris-pyrazolylborates and the triazacyclanones, the isoindoline nitrogen ligand atoms—whether pyrrole, pyridyl, or imine—cannot occupy three of the four positions in a tetrahedron simultaneously due to steric constraints. Further, while tris-pyrazolylborate and triazacyclanone ligands coordinate in a facial fashion in octahedral complexes, isoindolines are constrained to bind



in a meridional fashion. Isoindoline coordination generally occurs through the pyrrole and pyridyl nitrogen atoms, with the exception of one molybdenum(II) complex in which coordination through an imine nitrogen atom occurs.³ In this regard, the isoindoline anion is similar to a recently reported pincer-like quinolinylamido ligand that yields square planar complexes with Ni(II), Pd(II), and Pt(II).⁴

Only two systematic investigations of transition metal isoindoline complexes have been reported. In the first of these

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studies, Gagné and co-workers reported a series of six-coordinate bis(ligand) complexes of 4'-MeL⁻ (see above) with divalent metal ions of the first transition series (Mn²⁺–Zn²⁺).⁵ In the second study, Ittel and co-workers prepared analogous octahedral bis(ligand) complexes of 3'-MeL⁻ with Fe²⁺, Co²⁺, and Ni²⁺.⁶

In the present study, we wished to expand these earlier studies by examining under different reaction conditions how the tridentate isoindoline ligand, which as noted above is too rigid to occupy three of the four positions of a tetrahedron, interacts with Zn(II), a d¹⁰ metal ion that strongly prefers tetrahedral to square-planar coordination. We particularly wished to ascertain whether species other than the bis-octahedral complexes reported by Gagné and by Ittel are capable of existence in the absence of ancillary ligands. To this end, we have carried out the reaction of zinc perchlorate with 4'-MeL⁻ in 1:1 molar stoichiometry, to suppress formation of the known bis-octahedral complex Zn(4'-MeL)₂. The unexpected Zn(II) trinuclear reaction product, [Zn₃(4'-MeL)₄](ClO₄)₂, stands in marked contrast with the discrete, distorted trigonal bipyramidal, mononuclear copper(II) complex, [Cu(4'-MeL)(H₂O)₂](ClO₄), formed under analogous 1:1 stoichiometry reaction conditions. While only one complex of Zn(II) with isoindolines had been previously synthesized, a number of Cu(II) isoindoline complexes have been reported. Of the latter all but Cu(4'-MeL)₂ contain ancillary anionic ligands, for example, hydroxide,⁷ carbonate,⁷ and acetate,^{8,9} and exist in a variety of geometries including square planar, square pyramidal, and trigonal bipyramidal. All, however, exist with significant distortions from ideal geometry, and only one, [{Cu(4'-MeL)}₃{Cu(4'-MeL)O}(μ-OH)₃],⁷ contains a Cu(II) center comparable in structure to that of **2**.

Experimental Section

All starting materials and other chemicals were reagent grade and were commercially available. The 4'-MeLH ligand and the Zn-(4'-MeL)₂ complex were prepared following published procedures.^{5,10,11} ¹H NMR spectra in CDCl₃ were obtained on a Bruker AC-300 spectrometer. Infrared spectra were obtained on a Mattson Gemini spectrometer. Magnetic susceptibility was measured with a Johnson-Matthey magnetic susceptibility balance. EPR spectra were obtained on a Bruker CW-EPR spectrometer operating at X-band frequency. Elemental analyses were performed by Oneida Research Services and Quantitative Technologies.

Caution! Metal complexes containing organic ligands and perchlorate ion are potentially explosive and should be handled with care.

Synthesis of [Zn₃(4'-MeL)₄](ClO₄)₂·5H₂O (1**).** Methanolic tetra-*n*-butylammonium hydroxide solution (1.0 mL, 1.0 M) was added

Table 1. Crystallographic Data for Compounds **1** and **2**

cmpd	1	2
chemical formula	C ₈₀ H ₇₄ Cl ₂ N ₂₀ O ₁₃ Zn ₃	C ₂₀ H ₂₀ ClCuN ₅ O ₆
fw	1790.6	525.4
space group	<i>Ia</i> (var. No. 9)	<i>Pbcn</i> (No. 60)
<i>a</i> , Å	20.1604(2)	17.663(3)
<i>b</i> , Å	18.4326(3)	14.223(2)
<i>c</i> , Å	22.3174(4)	16.925(3)
β, deg	99.2710(10)	
<i>V</i> , Å ³	8185.0(2)	4251.9(13)
<i>Z</i>	4	8
<i>T</i> , °C	173(2)	154(2)
λ, Å	0.7107	0.7107
<i>D</i> _{calcd} , g cm ⁻³	1.45	1.64
μ, cm ⁻¹	1.012	1.203
<i>R</i> (<i>F</i> _o) ^a	0.0684	0.0410
<i>R</i> _w (<i>F</i> _o ²) ^a	0.224	0.099

^a Refinement by full-matrix least-squares on *F*² (all data); *R*_w for all data, *R* for *I* > 2σ(*I*); *R* = Σ(|*F*_o| - |*F*_c|)/Σ|*F*_o|; w*R*₂ = [Σw(*F*_o² - *F*_c²)²/Σw(*F*_o²)²]^{1/2}; w⁻¹ = σ²(*F*_o²) + (*LP*)² + *MP*, *P* = (*F*_o² + 2*F*_c²)/3, *L* = 0.0 and 0.1255, *M* = 28.1413 and 0.0 for **1** and **2**, respectively.

to 30 mL of a solution of 4'-MeLH (0.327 g, 1.0 mmol) in warm methanol. Solid Zn(ClO₄)₂·6H₂O (0.372 g, 1.0 mmol) was then added to the stirred solution. After filtration to remove traces of undissolved solids, slow cooling of the filtrate produced yellow crystals that proved suitable for X-ray diffraction studies. Yield: 0.288 g, 64%. IR(KBr): ν_{C=N/C=C} 1656, 1613, 1581, 1526, 1475 cm⁻¹; ν(ClO₄⁻) 1095 cm⁻¹. Anal. Calcd for C₈₀H₇₄N₂₀Cl₂O₁₃Zn₃: C, 53.66; H, 4.17; N, 15.65. Found: C, 53.21; H, 3.65; N, 15.40.

Synthesis of [Cu(4'-MeL)(H₂O)₂](ClO₄) (2**).** Methanolic tetra-*n*-butylammonium hydroxide solution (1.0 mL, 1.0 M) was added to 30 mL of a solution of 4'-MeLH (0.327 g, 1.0 mmol) in warm methanol. A warm solution of Cu(ClO₄)₂·6H₂O (0.370 g, 1.0 mmol) in 10 mL of methanol was then added to the stirred solution. After filtration to remove traces of undissolved solids, slow cooling of the filtrate produced green crystals that proved suitable for X-ray diffraction studies. Yield: 0.260 g, 50%. IR(KBr): ν_{C=N/C=C} 1619, 1573, 1523, 1470 cm⁻¹; ν(ClO₄⁻) 1108 cm⁻¹. Anal. Calcd for C₂₀H₂₀N₅CuClO₆: C, 45.73; H, 3.84; N, 13.33. Found: C, 45.95; H, 3.79; N, 13.42. μ_{eff} = 2.02 μ_B at 293 K.

X-ray Diffraction Studies of **1 and **2**.** X-ray diffraction data from crystals of **1** and **2** were recorded on a Bruker AXS SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Standard Bruker control (SMART) and integration (SAINT) software was employed, and Bruker SHELXTL^{12a} software was used for structure solution, refinement, and graphics. Selected crystallographic results and details of the X-ray diffraction experiments are listed in Table 1. The unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections in both cases.

Intensities were integrated from a series of frames (0.3° ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied for **1** and **2** by using SADABS.^{12b} A total of 24 845 reflections for **1** and 34 950 reflections for **2** were merged to provide final data sets containing 11 573 unique reflections (*R*_{int} = 0.050) for **1** and 4698 unique reflections (*R*_{int} = 0.0990) for **2**. The structures were solved by direct methods and refined (on *F*² using all data) by a full-matrix, weighted least-squares process.

The diffraction pattern of **1** was modeled as arising from two twin components related by an inversion center.^{12a} As listed in Table

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 (8) Bereman, R. D.; Shields, G. D.; Dorfman, J. R.; Bordner, J. J. *Inorg. Biochem.* **1983**, *19*, 75.
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1, the absolute structure parameter refined to 0.54 for the major twin component. Residual electron density in the case of **1** was best modeled as disordered occluded solvent. While both methanol and water were considered as possibilities for the occluded solvent, a model based on water yielded better *R* values and was used in the final refinement of the structure. On the basis of the electron density, oxygen atoms of five possible water molecules were located, but only one (O2) exhibited a site occupancy factor corresponding to a full oxygen atom. For the other four water oxygen atoms, final site occupancy factor values were 0.40 (O1), 0.95 (O3), 0.90 (O4), and 0.90 (O5). The estimated standard deviations in the atomic coordinates and derived metric parameters are relatively high; this may stem from the twinned nature of the structural model.

All non-hydrogen atoms in **2** were refined by using anisotropic displacement parameters. However, in **1** disorder involving water and perchlorate oxygen atoms precluded use of anisotropic displacement parameters for most of the oxygen atoms (except for the major components of O2 and O3). Hydrogen atoms of the coordinated water molecules in **2** were located in the electron density map and refined with isotropic displacement parameters, while all other hydrogen atoms in the final structural models for both **1** and **2** were placed in idealized positions.^{12a} Hydrogen atoms attached to carbon atoms were refined by using a riding model.^{12a} The final electron density maps showed features in the range from -1.35 (0.46 \AA from O1) to $+1.53$ (0.04 \AA from Zn1) $e \text{ \AA}^{-3}$ for **1** and from -0.94 to $+0.39 e \text{ \AA}^{-3}$ for **2**.

Results and Discussion

The products of the reactions of hydrated copper(II) perchlorate and zinc(II) perchlorate with the $4'$ -MeL⁻ anion in a 1:1 molar ratio in methanol are strikingly different. The 1:1 reaction with copper(II) produces the five-coordinate, distorted trigonal bipyramidal complex cation in **2**, which contains two water molecules as equatorial ligands. In contrast, the 1:1 reaction with Zn(II) produces the unexpected trinuclear complex in **1**, which contains only tetrahedrally coordinated zinc(II) atoms and no ligands other than the three $4'$ -MeL⁻ anions.

Coordination of Zn(II) by the isoindoline anion $4'$ -MeL⁻ was reported previously by Gagné and co-workers,⁵ who synthesized the bis-octahedral complex $\text{Zn}(4'\text{-MeL})_2$ by using a 2:1 molar ratio of $4'$ -MeL⁻ to $\text{Zn}(\text{ClO}_4)_2$. Unfortunately, the structure of that bis-ligand complex was not determined. It was readily apparent on examination of the NMR spectrum of **1**, however, that our 1:1 reaction had not produced Gagné's bis-ligand mononuclear complex. In fact, the ¹H NMR spectrum of **1**, which is shown in Figure 1, contains 12 resonance peaks, double the number expected for a mononuclear complex with C_{2v} symmetry. This spectrum implies that the pyridyl arms of $4'$ -MeL⁻ have dissimilar environments. In fact, when the reaction is performed with 1:1 stoichiometry, we have not detected any evidence for the presence of Gagné's bis-ligand complex.

The structure of **1**, as determined by single-crystal X-ray diffraction, confirms the complexity suggested by the NMR spectrum. Compound **1** contains discrete, trinuclear $[\text{Zn}_3(4'\text{-MeL})_4]^{2+}$ cations, one of which is shown in Figure 2. The cation is composed of two short helices of opposite hand that meet at Zn2. As shown, the helix coiling around Zn1 is

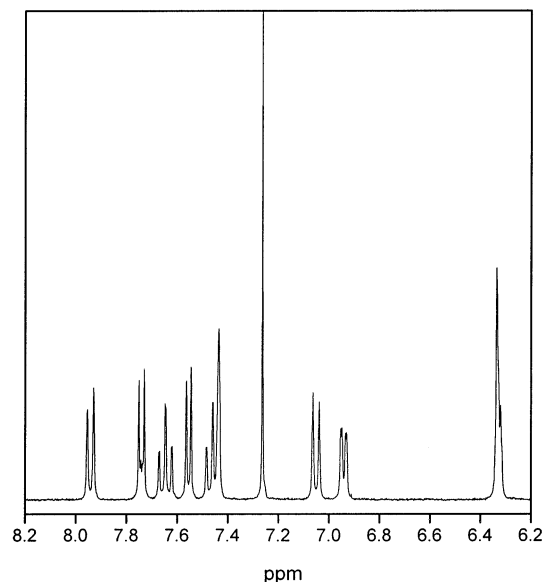


Figure 1. ¹H NMR spectrum (partial) of **1** in CDCl_3 .

left-handed, while the one coiling around Zn3 is right-handed. Despite this helicity, the three Zn(II) ions form a linear backbone of 179.8° for the molecule.

Each of the two outer zinc ions, Zn1 and Zn3, is coordinated in a roughly tetrahedral fashion with approximate C_2 symmetry by two different $4'$ -MeL⁻ ligands. Each of the $4'$ -MeL⁻ ligands bonds to an outer zinc atom as a *bidentate* ligand, with each ligand using a pyridyl nitrogen atom and a pyrrole nitrogen atom to coordinate to the metal. The pyridyl and pyrrole rings on each of the four isoindoline ligands that represent the donors to Zn1 and Zn3 are significantly canted relative to each other, with the angle between the best least-squares planes of the pyridyl and pyrrole rings within each ligand being on average $17(2)^\circ$.

The remaining pyridyl nitrogen atom of each of the four tridentate ligands is coordinated to the inner zinc ion, Zn2, which also has approximately tetrahedral site symmetry. Each of the pyridyl rings coordinated to Zn2 is rotated $72(5)^\circ$ on average from the best least-squares plane of the pyrrole ring to which it is attached.

Selected bond distances and angles for the unexpected trinuclear product in **1** are listed in Table 2. All C–C and C–N bond distances and internal bond angles for the ligands are consistent with bond lengths and angles in the six previously reported Cu(II) isoindoline structures.^{7–9,13,14} The Zn–N(pyridyl) distances to the inner and outer zinc ions are not significantly different, the average values for the two sets being $2.01(2)$ and $2.02(5) \text{ \AA}$, respectively. The average Zn–N pyrrole bond length of $1.93(5) \text{ \AA}$ is 0.09 \AA shorter than the average length of the outer Zn–N(pyridyl) bonds, which is consistent both with deprotonation of the pyrrole nitrogen and with prior crystallographic results.^{5,7–9,13,14}

The N–Zn–N bond angles about the inner zinc ion cluster about the ideal tetrahedral value of 109.5° , ranging from

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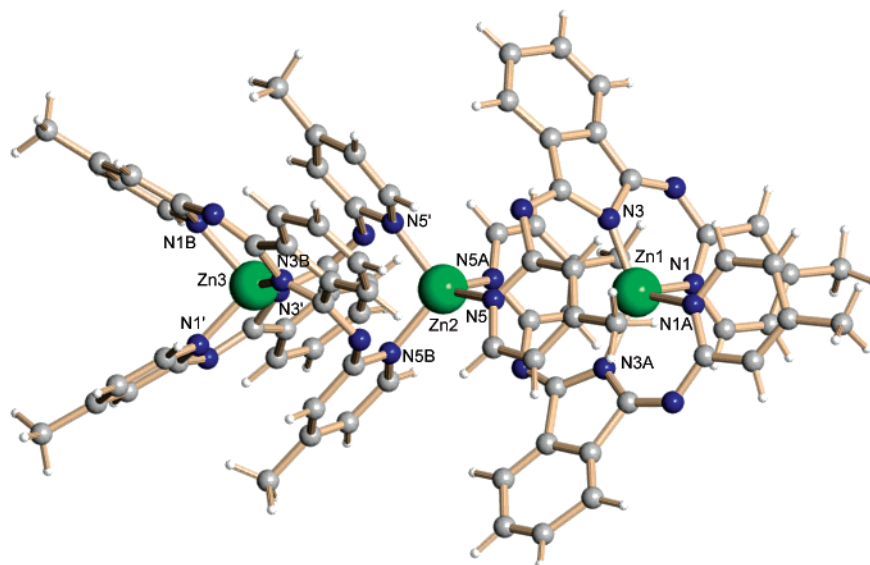


Figure 2. Ball and stick rendition of the structure of the $[\text{Zn}_3(4'\text{-MeL})_4]^{2+}$ cation in **1**.

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

Zn1–N3	1.88(2)	Zn2–N5	2.045(19)
Zn1–N3A	1.99(2)	Zn2–N5B	1.99(2)
Zn1–N1	2.00(2)	Zn2–N5'	2.02(2)
Zn1–N1A	2.07(2)	Zn2–N5A	1.99(2)
Zn3–N3B	1.94(2)	Zn3–N1'	1.96(3)
Zn3–N3'	1.91(2)	Zn3–N1B	2.07(2)
N3–Zn1–N3A	136.7(4)	N3B–Zn3–N3'	142.0(4)
N3–Zn1–N1	94.8(9)	N3B–Zn3–N1'	112.0(10)
N3A–Zn1–N1	113.7(9)	N3'–Zn3–N1'	94.2(9)
N3–Zn1–N1A	115.3(10)	N3B–Zn3–N1B	95.7(9)
N3A–Zn1–N1A	94.1(9)	N3'–Zn3–N1B	109.3(10)
N1–Zn1–N1A	96.1(4)	N1'–Zn3–N1B	95.2(4)
N5A–Zn2–N5B	112.4(9)	N5A–Zn2–N5	106.9(3)
N5A–Zn2–N5'	110.0(9)	N5B–Zn2–N5	111.9(9)
N5B–Zn2–N5'	103.6(3)	N5'–Zn2–N5	112.1(8)

^a Numbering for the nitrogen donor atoms in **1** is similar to that in **2** (see Figure 3). Zn1 is coordinated to N1,3 from one isoindoline and N1A,3A from another isoindoline. The pairs for Zn3 are N1',3' and N1B,3B. Zn2 is coordinated to N5,5A,5',5B.

103.6(3)° to 112.4(9)°. The N–Zn–N bond angles about the outer zinc atoms cover a much wider range from 94.1–(9)° to 142.0(4)°. The large deviations from idealized tetrahedral angles about the outer zinc atoms result from the steric constraints imposed by the isoindoline ligands.

Each of the four pyridyl rings attached to the inner zinc atom (Zn2) lies roughly parallel to one or another of the pyrrole rings bound to Zn1 or Zn3, with an average pyridyl–pyrrole ring separation of 3.24(9) Å. This suggests that interring π -stacking interactions are present and contribute to the stability of the trinuclear cation relative to mononuclear complexes. The trinuclear cation does not appear to be involved in hydrogen bonding to the occluded solvent molecules.

The ¹H NMR spectrum of **1** in CDCl₃ is shown in Figure 1. The spectrum clearly demonstrates that the structural integrity of the trinuclear cation is preserved in solution. Two sets of resonances per chemically distinct proton are observed, which is consistent with Zn1 and Zn3 having symmetry-equivalent environments in solution. The assignments listed in Table 3 were made with the use of H,H-

Table 3. ¹H NMR Chemical Shifts for Zn(II) Complexes^a

proton	1	Zn(4'-MeL) ₂
H _a	7.92 (m) outer ^b	8.09 (m)
	7.05 (m) inner ^c	
H _b	7.64 (m) outer	7.66 (m)
	7.44 (m) inner	
H _d	7.54 (d) outer	7.97 (d)
	7.72 (d) inner	
H _e	6.91 (m) outer	6.48 (m)
	6.31 (m) inner	
H _f	7.42 (s) outer	7.13 (s)
	6.32 (s) inner	
CH ₃	2.43 (s) outer	2.17 (s)
	1.76 (s) inner	

^a Chemical shifts in ppm relative to TMS at 294 K. ^b Protons proximal to Zn(1) and Zn(3) in **1**. ^c Protons proximal to Zn(2) in **1**.

COSY, homonuclear decoupling, and by comparison to the previously assigned ¹H spectrum of Zn(4'-MeL)₂,⁵ the chemical shifts for which are also listed in Table 3. Protons that are proximal to Zn2 are labeled as *inner* protons and those proximal to Zn1 or Zn3 are labeled as *outer* protons. Identification of each set, that is, which set is inner and which is outer, was made by reference to molecular models of **1** and predicted ring current, shielding effects that inner protons, especially methyl protons and H_a, would experience. For example, the four outer –CH₃ groups (δ = 2.43 ppm) are directed away from the trinuclear cation and have no immediate neighbors, whereas each of the four inner –CH₃ groups (δ = 1.76 ppm) sit above and in close proximity to the π -cloud of a nearby pyridyl ring.

The structural motif encountered in the complex cation of **1**—trinuclear, linear array of three Zn(II) atoms, all three Zn(II) atoms four-coordinate and exhibiting approximately tetrahedral coordination—is highly unusual for Zn(II); it has been found in only one other complex.^{15,16} It was certainly not an expected result here. The 4'-MeL[–] ligand, which appears best suited for planar, tridentate coordination, might have been expected to form a five-coordinate, trigonal bipyramidal complex with Zn(II) such as Zn(terpy)Cl₂ (terpy

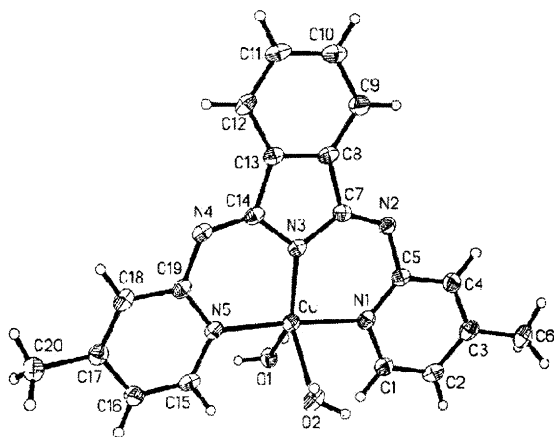


Figure 3. Thermal ellipsoid plot (50% probability) showing the structure and numbering scheme of the $[\text{Cu}(4'\text{-MeL}(\text{H}_2\text{O})_2)^+]$ cation in **2**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **2**

Cu–N3	1.904(2)	Cu–O1	2.094(2)
Cu–N5	1.975(2)	Cu–O2	2.239(2)
Cu–N1	1.983(2)		
N3–Cu–N5	91.07(10)	N1–Cu–O1	88.43(9)
N3–Cu–N1	91.23(9)	N3–Cu–O2	120.69(9)
N5–Cu–N1	176.00(9)	N5–Cu–O2	86.12(9)
N3–Cu–O1	136.20(9)	N1–Cu–O2	89.80(9)
N5–Cu–O1	92.17(9)	O1–Cu–O2	103.19(9)

$= 2,2':6',2''\text{-terpyridine}$).¹⁷ Alternatively, it might also have been expected to form a bis-octahedral complex, $\text{Zn}(4'\text{-MeL})_2$, regardless of the mole ratio of reactants.

The surprising formation of the trinuclear complex in **1** in solution and its preservation in the solid state may be due in part to the intramolecular inter-ring π -stacking interactions between the pyrrole and pyridine rings noted above. It remains to be seen, however, whether the trinuclear structural motif is unique to the group 12 triad metals¹⁸ or whether other divalent transition metal ions, for example, the similarly sized Co(II) ion, will also form trinuclear, tetrahedrally coordinated complexes with $4'\text{-MeL}^-$.

In contrast to the trinuclear Zn(II) complex, a 1:1 molar ratio of Cu(II) and $4'\text{-MeL}^-$ produces a discrete mononuclear roughly trigonal bipyramidal complex cation, $[\text{Cu}(4'\text{-MeL})(\text{H}_2\text{O})_2]^+$. A trinuclear copper(II) complex is presumably less favorable since the stabilization available from intramolecular, inter-ring π -stacking interactions (see above) is unable to overcome the unfavorable energetics associated with Cu(II) tetrahedral coordination.

The structure of the $[\text{Cu}(4'\text{-MeL})(\text{H}_2\text{O})_2]^+$ complex cation is shown in Figure 3, while selected bond lengths and angles are listed in Table 4. The isoindoline ligand is nearly planar, with the two pyridyl rings slightly canted by 5.8° and 3.0° with respect to the center pyrrole ring. All C–C and C–N bond distances and all internal bond angles for the ligand

are consistent with those found in **1** and the six related Cu(II) isoindoline complexes that have been previously reported.^{7–9,13,14} The structure of the cation in **2** most closely resembles a distorted trigonal bipyramid in which water molecules occupy two of the three equatorial positions. The bond between the copper(II) atom and the deprotonated pyrrole nitrogen atom of the $4'\text{-MeL}^-$ ligand (Cu–N3 = 1.904(2) Å) is approximately 0.08 Å shorter than the Cu–N(pyridyl) bonds, as expected.^{7–9,13,14} The Cu–O bond lengths of 2.094(2) and 2.239(2) Å are surprisingly different from one another, but are close to the bond lengths for equatorially coordinated water observed in the distorted trigonal bipyramidal 1,10-phenanthroline complexes $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{BF}_4)_2$ (Cu–O = 2.23 Å) and $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{NO}_3)_2$ (Cu–O = 2.18 Å).^{19,20} The Cu(II) ion is only 0.003 Å removed from the equatorial plane formed by N3, O1, and O2. The pyridyl nitrogen atoms N1 and N5 thus occupy axial positions, with N1–Cu–N5 nearly linear at $176.00(9)^\circ$. The angular distortions about copper(II) within the equatorial plane are significant, with the largest of the three angles being $136.20(9)^\circ$ and the smallest $103.19(9)^\circ$.

We believe that these metric parameters demand description of the cation of **2** as an equatorially distorted, trigonal bipyramidal complex. Addison et al.²¹ have defined a structural parameter τ to show the percent correspondence of a five-coordinate complex to one or the other of two ideal geometries, square pyramidal or trigonal bipyramidal ($\tau = 0$ would denote ideal square pyramidal; $\tau = 1$ would denote ideal trigonal bipyramidal). In defining the τ parameter, Addison et al. assumed that the complex under consideration would have C_{2v} symmetry and a structure intermediate between the ideal trigonal bipyramidal and ideal square pyramidal extremes along the pathway defined by the Berry pseudorotation process.²²

In the case of the complex cation in **2**, the significant angular distortions in the equatorial plane mean that $[\text{Cu}(4'\text{-MeL})(\text{H}_2\text{O})_2]^+$ does not satisfy these assumptions. Certainly the value of $\tau = 0.66$ that can be calculated from the structural parameters of **2** implies somewhat more trigonal bipyramidal character than square pyramidal character, but the quantitative meaning of the τ value is questionable, given the metric deviations from Addison's assumptions. Others have recently voiced a similar concern regarding the general applicability of τ values for five-coordinate Cu(II) complexes.²³

Prior to this work, six Cu(II) isoindoline complexes had been structurally characterized,^{7–9,13,14} all contained ancillary anionic ligands. The structural theme common to all six complexes is that an ancillary ligand, even one as small as H_2O , cannot coordinate trans to the pyrrole nitrogen atom without significant out-of-plane displacement. In addition,

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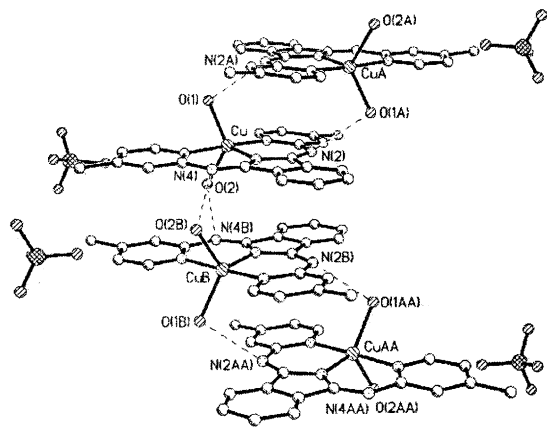


Figure 4. Packing plot of $[\text{Cu}(4'\text{-MeL})(\text{H}_2\text{O})_2]^+$ cations in **2** showing hydrogen-bonding contacts.

ruffling of the isoindoline framework was also observed, due to unfavorable steric interactions between the donor atom of the ancillary ligand and the hydrogen atoms on C1 and C15 of the isoindoline ligand. The distorted trigonal bipyramidal geometry observed for $[\text{Cu}(4'\text{-MeL})(\text{H}_2\text{O})_2]^+$ in **2** is closely mirrored in one of these six complexes, the tetranuclear chain $[\{\text{Cu}(4'\text{-MeL})\}_3\{\text{Cu}(4'\text{-MeL})\text{O}\}(\mu\text{-OH})_3]$.⁷ In that complex, the site symmetries and metric details associated with the two inner Cu(II) ions closely resemble the structural parameters in **2** (allowing for the fact that both of these copper(II) atoms in the tetranuclear complex have bridging hydroxide ligands attached equatorially).

The cations in **2** are linked together in a three-dimensional network by hydrogen bonding and by π - π interactions.

Intermolecular hydrogen bonding between H_2O ligands and imine nitrogen atoms of isoindoline ligands ($\text{O1}\cdots\text{N2} = 2.763(3)$ Å, $\text{O2}\cdots\text{N4} = 2.856(3)$ Å) results in a one-dimensional chain (see Figure 4). In addition, π - π interactions may contribute to the stability of this chain since inter-ring separations vary from 3.27(8) Å (pyrrole-pyrrole) to 3.38(11) Å (pyrrole-pyridyl). The chains are connected by hydrogen bonding between coordinated water and perchlorate anions. The rhombic EPR spectrum ($g = 2.02, 2.09, 2.22$) of a powdered sample at 132 K is consistent with spectra of other trigonal bipyramidal Cu(II) complexes.²⁴ No evidence for magnetic exchange coupling between Cu(II) ions was found.

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Supporting Information Available: X-ray crystallographic files in CIF format for $[\text{Zn}_3(4'\text{-MeL})_4](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ and $[\text{Cu}(4'\text{-MeL})(\text{H}_2\text{O})_2]\text{ClO}_4$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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