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Thermoluminescent Antimony-Supported Copper-lodo Cuboids: Approaching NIR Emission via High Crystallographic Symmetry

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Supporting Information

ABSTRACT: We report the syntheses, structures, and luminescence properties of a series of copper-iodo cuboids supported by L-type antimony ligands. The cuboids are of general formula $[(SbR_3)_4Cu_4(I)_4]$ (1-4, 8), where SbR₃ is a series of homoleptic and heteroleptic stibines containing both phenyl and a variety of alkyl substituents (R = Cy, 'Pr, 'Bu, Ph); triphenyl, 'Pr₂Ph, and Me₂Ph stibines resulted in the formation of dimers of type $[(SbR_3)_4(Cu)_2(I)_2]$ (5–7). While similar luminescent copper-halide cubes have been studied, the corresponding "heavy-atom" congeners have not been studied, and ligation of such heavy-atom moieties is often associated with long-lived triplet states and low-energy absorption and emission profiles. Overall, two obligate



parameters are found to imbue NIR emission: (i) short Cu-Cu bonds and (ii) high crystallographic symmetry; both of these properties are found only in $[(Sb^iPr_3)_4Cu_4(I)_4]$ (1, in I23; $\lambda_{em} = 711$ nm). The correlation between NIR emission and high crystallographic symmetry (which intrinsically includes high molecular symmetry)-versus only molecular symmetry-is confirmed by the counterexample of the *molecularly* symmetric ^tBu-substituted cuboid $[(Sb^tBu_3)_4Cu_4(I)_4]$ (3, $\lambda_{em} = 588$ nm, in R-3), which crystallizes in the lower symmetry trigonal space group. Despite the indication that the stronger donor strength of the SbⁱBu₃ ligand should red-shift emission beyond that of the SbⁱPr₃-supported cuboid, the emission of 3 is limited to the visible region. To further demonstrate the connection between structural parameters and emission intensity, X-ray structures for 1 and 3 were collected between 100 and 300 K. Lastly, DFT calculations for 1 on its singlet (S_0) and excited triplet state (T_1) demonstrate two key factors necessary for low-energy NIR emission: (i) a significant contraction of the interconnected Cu_4 intermetallic contacts [~2.45 \rightarrow 2.35 Å] and (ii) highly delocalized (and therefore low-energy) A₁ symmetry HOMO/LUMO orbitals from which the emission occurs. Thus, any molecular or crystallographic distortion of the Cu4 core precludes the formation of highly symmetric (and low-energy) HOMO/LUMO orbitals in T₁, thereby inhibiting low-energy NIR emission.

INTRODUCTION

Transition metal complexes and clusters with luminescent properties have found utility in fields ranging from OLEDs, bioimaging devices, and pressure-sensing devices (mechanochromism).¹⁻³ In addition, the discovery of new molecules and materials that achieve NIR emission is desirable for applications such as deep-tissue bioimaging, photodynamic therapy, and novel two-photon and triplet-transfer solar technologies.⁴⁻⁶ Long-lived NIR emission (phosphorescence) is difficult to achieve due to the closer proximity of lower-lying triplet states to thermally excited ground states.^{7,8} Additionally, the presence of high energy oscillators (such as O-H bonds) causes vibrational quenching in NIR emitters and limits long-lived emissions.^{9,10} While a number of examples of organicbased dyes and sensors for NIR emission and sensing have been reported,^{11,12} these are largely limited to short-lived fluorescence rather than longer-lived phosphorescence, which has a higher possibility for persistent emission past initial excitation.¹³ The use of transition metals—and, in conjunction, heavy atoms to enhance intersystem crossing-could afford

new classes of bright, long-lived phosphors for biological and energy applications. However, there is a need for fundamental studies of transition metal-based NIR phosphorescent complexes, clusters, and materials.

In particular, copper-based complexes are intriguing for their low cost and relative stability. Luminescent copper complexes exist in the form of monomers, dimers, tetramers, and polymeric species-and their emission wavelengths span the entire visible spectrum.^{14,15} An interesting subset of luminescent copper-halide compounds are the cubes with general structure $Cu_4X_4L_4$ (where X = halide; L = pnictogen ligand). These complexes exhibit a unique property known as luminescent thermochromism, in which emission intensity and energy fluctuate as a function of temperature. First discovered by Hardt,¹⁶ luminescent thermochromism is classically explained as being derived from two triplet excited states: one originating at the center of the copper cluster $({}^{3}CC)$ and

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one originating from charge transfer from the halide to the ligand (³XLCT).¹⁷ Typically, a low energy (LE) band is observed at room temperature and corresponds to the CC transition, whereas at low temperatures, this band is abolished and the presence of a high energy (HE) band emerges, corresponding to the XLCT process. Notably, neither band (specifically, the LE band) has been reported to occur in the near-infrared (NIR) region.

Among published thermochromic copper cubes, the Cu₄I₄ core remains constant for the most part, but the supporting ligand can be modulated. Photoactive clusters have been reported containing nitrogen, phosphorus, sulfur, and arsenic ligands; however, not all have been investigated for their luminescent properties.^{18–21} Our research has focused on utilizing antimony-based supporting ligands with the aim of modulating structural parameters²² and red-shifting emission and absorption features due to the so-called "heavy atom effect".^{23–25} Additionally, our previous communication²² demonstrated that the relatively weak σ donor strength of Sb ligands allows for long Cu–Sb bonds and—as a result—short Cu…Cu contacts that are within 2× the van der Waals radius.^{26,27}

Extensive literature on phosphine-supported Cu_4I_4 cubes has elucidated a number of structure–activity design principles. In general, phosphine-supported cubes exhibit luminescent properties at ambient temperatures, regardless (without known exception) of the phosphine substituents.¹⁷ Second, the emissive properties of these cubes are dependent on temperature–primarily via thermochromism; that is, two competing emissive states (LE = 500–600 nm, HE = 400– 500 nm; see paragraphs above) can be proportionally accessed depending on the temperature. Studies have shown that thermochromic properties (i.e., the presence of the HE XLCT band) are dependent on the identity and number of phosphine substituents.

To determine the effect of a "heavy atom" approach, we synthesized and reported the luminescent properties of antimony-supported cluster 1,²² namely $Cu_4(I)_4(Sb^iPr_3)_4$. Cluster 1 exhibits three luminescence properties that distinguish it from the majority of phosphine clusters: (*i*) no HE emission band is observed (not thermochromic = desired for pure LE emitters); (*ii*) the emission is shifted into the NIR at 710 nm; and (*iii*) the NIR luminescence is only observed at low temperatures. Regarding point (*i*), based on the discussion above (phenyl versus alkyl substituents), the lack of a HE band is due simply to the lack of phenyl substituents on antimony (precludes XLCT). While the resolution to point (*iii*) remained ambiguous (addressed herein, vide infra), the NIR LE emission from 1 was ascribed to structural features as follows:

The close Cu^{•••}Cu contacts in the ground state of 1 gave rise to a pseudometallic Cu₄ tetrahedron at the core of the cuboid, with a 2.76 Å distances between all copper ions (crystallographically defined) at 100 K. Notably, this distance is less than 2× the van der Waals radius of copper (~2.80 Å). In this report,²² crystal structure solutions for 1 at varying temperatures between 100 and 300 K revealed a distinct structure– emission correlation between shorter Cu^{•••}Cu distances [low T: 2.761(3) \rightarrow 2.836(4) Å, high T] and increased luminescence. Indeed, as the Cu^{•••}Cu distance crossed 2× the van der Waals radius of copper (~2.80 Å), the emission *intensity* exponentially increased. It is also notable that the Cu^{•••}Cu distance found in 1 (~2.76 Å) is distinctly shorter than the average Cu···Cu distance found in phosphinesupported cubes ($\sim 2.85-3.15$). At first glance, these results suggest that close intermetallic contacts are required for shifting the emission energy to the NIR. In contrast, our own data for 1 regarding the structure—emission correlation (temperature dependence) suggests that the Cu···Cu distance controls the emission *intensity* not the emission *energy*. Thus, based on all of the information presented above, our research goals were to (*i*) shift the emission profile further into the NIR, (*ii*) resolve the apparent paradox involving the correlation between Cu···Cu contacts and emission energy/intensity, and (*iii*) develop a fundamental understanding of the correlations between ligand identity, cluster structure, and emission properties.

It is known (and confirmed in our work) that SbPh₃ does not form cube or cuboid structures, and thus further ligand design and synthetic rationale were required to access the cuboid motif. Therefore, to fully elucidate the structureactivity relationships within this class of Sb₄Cu₄I₄ clusters, it was necessary to synthesize and employ a wide range of antimony-based ligands-including those with and without phenyl units, with larger and smaller cone angles, with stronger or weaker donor strength, as well as with varying extents of symmetry. In this work, we report the syntheses, structures, and solid-state luminescence properties of a series of antimonysupported copper cuboids (and dimers) based on homoleptic and heteroleptic SbR₃ ligands (where R = Me, ^{*i*}Pr, ^{*t*}Bu, Cy, Ph). A thorough analysis of the effect of ligand sterics, as well as molecular and crystallographic symmetries, is presented, and the experimental findings are supported by DFT calculations regarding the enigmatic origin of low energy luminescence.

EXPERIMENTAL SECTION

Reagents and General Procedures. All reactions were conducted under a dry dinitrogen atmosphere (Schlenk line, ligand syntheses) or under an argon atmosphere in a drybox (metalations). Solvents were HPLC-grade and purified over alumina using a Pure Process Technology solvent purification system. Deuterated solvents were purchased from Cambridge Laboratories and used without further purification, and the freeze-pump-thaw technique was used to degas deuterated solvents as necessary. The starting materials trichloroantimony and triphenylantimony were purchased from Strem Chemicals and used without further purification. Magnesium turnings (Acros), iodine crystals (Acros), 2-chloropropane (Sigma-Aldrich), iodomethane (Oakwood Chemical), tert-butyl magnesium chloride 2.0 M in Et₂O (Sigma-Aldrich), cyclohexyl magnesium chloride 1.0 Min 2-MeTHF (Alfa Aesar), copper iodide (Strem Chemicals), and fluorobenzene (FPh, Oakwood Chemical) were purchased and used as received without further purification.

Ligand Syntheses. Safety Precaution. Alkyl-substituted antimony ligands are volatile and air-sensitive and can be pyrophoric, and they must be handled with caution under inert atmosphere. The corresponding metal complexes are also highly air-sensitive and sometimes pyrophoric and must be handled with similar care.

Diisopropylphenylantimony (Sb[']Pr₂Ph). Trichloroantimony (5.64 g, 24.7 mmol) and triphenylantimony (4.36 g, 12.4 mmol) were stirred together solvent-free for 3 h to afford dichlorophenylantimony (10 g, 37.06 mmol) in quantitative yield. Magnesium turnings (2.70 g, 111 mmol) were activated with iodine (0.01 g, 0.04 mmol) and heated for 30 min under vacuum. Dry Et₂O (125 mL) was added to the flask, and 1,2-dibromoethane (0.22 g, 1.16 mmol) was subsequently added. Next, 2-chloropropane (7.27 g, 92.6 mmol) was added to the flask at 0 °C and the reaction was stirred overnight. The solution was filtered. The SbCl₂Ph was then dissolved in Et₂O (90 mL) and added dropwise to the filtered Grignard solution, and the reaction was refluxed for 3 h. The solution was then quenched with degassed water (50 mL). Under inert atmosphere, the organic layer was separated and dried over sodium sulfate and then filtered. The solvent was removed *in vacuo* to afford a colorless oil. A fractional distillation was performed, which first distilled trace amounts of SbⁱPr₃ (75 °C, 0.01 mmHg), followed by the desired product (120 °C, 0.01 mmHg) as a colorless oil (4.7 g, 16.48 mmol). Yield: 45%. ¹H NMR (CDCl₃): δ 1.32 (d 6H, –CH₃), 1.22 (d 6H, –CH₃), 2.08 (hept 2H, –CH), 7.51 (mult 2H, aromatic CH), 7.32 (mult 3H, aromatic CH). ¹³C NMR (CDCl₃): δ = 20.1, 21.9, 22.1, 128.3, 128.5, 136.5.

Dimethylphenylantimony (SbMe₂Ph). The methylmagnesiumiodide Grignard solution was generated in situ in the same manner as above with magnesium turnings (4.08 g, 168 mmol) and iodomethane (19.7 g, 139 mmol). Trichloroantimony (8.45 g, 37.1 mmol) and triphenylantimony (6.55 g, 18.5 mmol) were stirred together (no solvent) for 3 h to afford dichlorophenylantimony (15.0 g, 55.6 mmol) in quantitative yield. The SbCl₂Ph was dissolved in Et₂O (125 mL) and added dropwise to the filtered Grignard solution, and the reaction was refluxed for 3 h. The solution was then quenched with degassed water (70 mL). Under inert atmosphere, the organic layer was separated, dried over sodium sulfate, and filtered. The solvent was removed in vacuo to produce a slightly yellow oil. A distillation was performed to afford the desired product (50 °C, 0.01 mmHg) as a colorless oil (8.9 g, 39.0 mmol). Yield: 70%. ¹H NMR $(CDCl_3)$: δ 0.97 (s 6H, $-CH_3$), 7.55 (mult 2H, aromatic CH), 7.32 (mult 3H, aromatic CH). ¹³C NMR (CDCl_3): δ = 128.3, 128.6, 135.0, 137.5.

Ditertbutylphenylantimony (Sb^t**Bu**₂**Ph**). *tert*-Butyl magnesium chloride solution (2.0 M in Et₂O, 20.8 mL, 41.7 mmol) was added dropwise to a stirring solution of SbCl₂Ph in Et₂O (5 g, 18.5 mmol, 125 mL) on ice. The solution was refluxed for 3 h and then allowed to cool to room temperature. The solution was quenched with degassed water (70 mL). Under inert atmosphere, the organic layer was separated, dried over sodium sulfate, and filtered. The solvent was removed *in vacuo* to produce a slightly yellow oil. A distillation was performed at 130 °C to afford the product as a colorless clear oil (1.7 g, 5.4 mmol). Yield: 30%. ¹H NMR (CDCl₃): 1.31 (s 18H, $-CH_3$), 7.31 (mult 3H, aromatic CH), 7.61 (mult 2H, aromatic CH). ¹³C NMR (CDCl₃): δ = 31.6, 34.6, 128.4, 129.1, 135.6, 137.5.

Tri-tert-butylantimony (Sb'Bu₃). A solution of SbCl₃ in Et₂O (3 g, 13.1 mmol, 100 mL) was added dropwise to a stirring solution of *tert*-butyl magnesium chloride (2.0 M in Et₂O, 26.3 mL, 52.6 mmol) on ice. The solution was refluxed for 3 h and then allowed to cool to room temperature. The solution was quenched with degassed water (70 mL). Under inert atmosphere, the organic layer was separated, dried over sodium sulfate, and filtered. The solvent was removed *in vacuo* to produce a slightly yellow oil. A distillation was performed at 100 °C to provide the product as a slightly yellow oil (1.0 g, 3.4 mmol). Yield: 26%. ¹H NMR (CDCl₃): 1.33 (s 18H, $-CH_3$). ¹³C NMR (CDCl₃): δ = 32.3, 34.7.

Tricyclohexylantimony (SbCy₃). A solution of SbCl₃ in Et₂O (2.5 g, 10.9 mmol, 100 mL) was added dropwise to a stirring solution of cyclohexyl magnesium chloride (1.0 M in Et₂O, 38.3 mL, 38.3 mmol) on ice. The solution was refluxed for 3 h and then allowed to cool to room temperature. The solution was quenched with degassed water (70 mL). Under inert atmosphere, the organic layer was separated, dried over sodium sulfate, and filtered. The solvent was removed *in vacuo* to produce a white solid (2.7 g, 7.2 mmol). Yield: 66%. ¹H NMR (CDCl₃): 1.31 (mult 12H, $-CH_2$), 1.48 (mult 3H, -CH), 1.73 (mult 18H, $-CH_2$). ¹³C NMR (CDCl₃): $\delta = 27.1$, 28.2, 29.0, 32.9.

Synthesis of the Metal Complexes. $Cu(l)_4(Sb^lPr_3)_4$ (1). This cluster was previously synthesized and reported in our previous communication.²²

 $Cu_4(l)_4(SbCy_3)_4$ (2). Copper iodide (0.14 g, 0.74 mmol) was added to SbCy₃ (0.28 g, 0.74 mmol) in 15 mL of fluorobenzene at -20 °C under argon atmosphere. The reaction was allowed to warm to room temperature, and the reaction mixture was stirred overnight. The clear, slightly yellow solution was filtered, and the solvent was removed in vacuo to afford a light yellow oil and a white precipitate. The product was washed several times with pentane to remove the oil, leaving the desired product as a white solid (0.15 g, 0.07 mmol). Yield: 36%. Crystals suitable for X-ray crystallography were obtained via slow vapor diffusion of pentane into a DCM solution of the product at -20 °C. ¹H NMR: (CDCl₃): 1.27 (mult 18H, $-CH_2$), 1.73 (mult 12H, $-CH_2$), 1.95 (mult 3H, -CH). ¹³C NMR (CDCl₃): $\delta = 26.9$, 29.0, 29.2, 32.3. Anal. cald (% wt.) for Cu₄I₄Sb₄C₇₂H₁₃₂: C, 38.49; H, 5.92. Found: C, 38.37; H, 5.95.

 $Cu_4(l)_4(Sb^tBu_3)_4$ (**3**). Copper iodide (0.08 g, 0.42 mmol) was added to Sb^tBu₃ (0.5 g, 1.7 mmol) in 15 mL of fluorobenzene at -20 °C under argon atmosphere. The reaction was allowed to warm to room temperature, and the reaction mixture was stirred overnight to provide a colorless solution and a white precipitate. The solution was decanted, and the white solid was washed several times with pentane to remove impurities, leaving behind the purified desired product as a white solid (0.051 g, 0.03 mmol). Yield: 25%. Crystals suitable for Xray crystallography were obtained via slow vapor diffusion of pentane into a DCM solution of the product at -20 °C. ¹H NMR (CDCl₃): 1.47 (s 18H, $-CH_3$). ¹³C NMR (CDCl₃): δ = 32.6, 35.6. Anal. cald (% wt.) for Cu₄I₄Sb₄C₄₈H₁₀₈: C, 29.81; H, 5.63. Found: C, 29.78; H, 5.74.

 $Cu_4(l)_4(Sb^tBu_2Ph)_4$ (4). Copper iodide (0.08 g, 0.42 mmol) was added to Sb^tBu₂Ph (0.53 g, 1.7 mmol) in 15 mL of fluorobenzene at -20 °C under argon atmosphere. The reaction was allowed to warm to room temperature, and the reaction mixture was stirred overnight to yield a clear, colorless solution. The solution was filtered, and the solvent was removed in vacuo to generate a light yellow oil. The oil was washed several times with pentane, which precipitated out the product as a white solid (0.065 g, 0.03 mmol). Yield: 31%. Crystals suitable for X-ray crystallography were obtained via slow vapor diffusion of pentane into a DCM solution of the product at -20 °C. ¹H NMR (CDCl₃): 1.49 (s 18H, $-CH_3$), 7.33 (mult 3H, aromatic CH), 7.90 (mult 2H, aromatic CH). ¹³C NMR (CDCl₃): $\delta = 32.0$, 34.7, 128.5, 129.1, 134.0, 138.1. Anal. cald (% wt.) for Cu₄I₄Sb₄C₅₆H₉₂: C, 33.39; H, 4.60. Found: C, 33.17; H, 4.62.

 $Cu_2(l)_2(Sb^{i}Pr_2Ph)_4$ (5). Copper iodide (0.04 g, 0.22 mmol) was added to SbⁱPr_2Ph (0.26 g, 0.88 mmol) in 15 mL of fluorobenzene at -20 °C under argon atmosphere. The reaction was allowed to warm to room temperature, and the reaction mixture was stirred overnight, yielding a clear, colorless solution. The solvent was removed in vacuo to yield a light brown oil and a white precipitate. The oil was dissolved into pentane and placed into the freezer at -20 °C to yield the dimer product as a white crystalline solid (0.03 g, 0.02 mmol). Yield: 16%. Crystals suitable for X-ray crystallography were obtained via slow evaporation of a pentane solution of the product at -20 °C. ¹H NMR: δ 1.39 (d 6H, $-CH_3$), 1.28 (d 6H, $-CH_3$), 2.24 (hept 2H, -CH), 7.60 (mult 2H, aromatic CH), 7.32 (mult 3H, aromatic CH). ¹³C NMR (CDCl₃): δ = 20.1, 21.9, 128.5, 128.8, 136.3, 136.5. Anal. cald (% wt.) for Cu₂I₂Sb₄C₄₈H₇₆: C, 37.90; H, 5.04. Found: C, 37.46; H, 4.56.

 $Cu_2(l)_2(SbMe_2Ph)_4$ (6). Copper iodide (0.14 g, 0.75 mmol) was added to SbMe_2Ph (0.68 g, 3.00 mmol) in 15 mL of fluorobenzene at -20 °C under argon atmosphere. The reaction was allowed to warm to room temperature, and the reaction mixture was stirred overnight to generate a clear, colorless solution. The solvent was removed in vacuo to afford a clear oil. The product was dissolved into pentane and placed into the freezer at -20 °C to yield the product as a white solid (0.11 g, 0.08 mmol). Yield: 23%. Crystals suitable for X-ray crystallography were obtained via slow evaporation of a pentane solution of the product at -20 °C. ¹H NMR: (C₆D₆): 0.85 (s 6H, $-CH_3$), 7.10 (mult 3H, aromatic CH), 7.53 (mult 2H, aromatic CH). ¹³C NMR (CDCl₃): $\delta = -1.7$, 128.8, 128.9, 134.7, 135.1. Anal. cald (% wt.) for Cu₂I₂Sb₄C₃₂H₄₄: C, 29.64; H, 3.42. Found: C, 29.41; H, 3.47.

Cu₂(l)₂(SbPh₃)₄ (7). The product Cu₂(I)₂(SbPh₃)₄ was prepared according to a published procedure.²⁸ ¹H NMR: (C₆D₆): 7.23 (mult 2H, aromatic CH), 7.34 (mult 3H, aromatic CH). ¹³C NMR (CDCl₃): δ = 128.8, 129.1, 136.4, 138.5. Anal. cald (% wt.) for Cu₂I₂Sb₄C₇₂H₆₀: C, 48.23; H, 3.37. Found: C, 45.10; H, 3.25.

 $Cu_4(l)_4(Sb^iPr_2Ph)_4$ (8). Copper iodide (0.04 g, 0.22 mmol) was added to SbⁱPr_2Ph (0.06 g, 0.22 mmol) in 15 mL of fluorobenzene at

-20 °C under an inert argon atmosphere. The reaction was allowed to warm to room temperature, and the reaction mixture was stirred overnight to yield a clear, colorless solution. The solvent was removed in vacuo to yield a light brown oil and a white precipitate. The product was washed several times with pentane to remove the oil, leaving the desired product as a white solid (0.09 g, 0.04 mmol). Yield: 51%. ¹H NMR: δ 1.48 (d 6H, $-CH_3$), 1.35 (d 6H, $-CH_3$), 2.38 (hept 2H, -CH), 7.70 (mult 2H, aromatic CH), 7.33 (mult 3H, aromatic CH). ¹³C NMR (CDCl₃): δ = 20.8, 21.9, 128.6, 128.9, 136.4, 136.8. Anal. cald (% wt.) for Cu₄I₄Sb₄C₄₈H₇₆: C, 30.31; H, 4.03. Found: C, 29.79; H, 3.98.

Physical Measurements. NMR (¹H and ¹³C) measurements were obtained using a 500 MHz Bruker AVANCE III NMR; CDCl₃ was referenced to 7.26 and 77.2 ppm for ¹H and ¹³C spectra, respectively. Elemental analyses (C, H) were performed by Midwest Microlab, IN. Absorption spectra were recorded on a Varian Cary 6000i UV-vis-NIR spectrophotometer using Starna Quartz Fluorometer Cells with path lengths of 10 mm. Luminescence measurements were recorded on a Photon Technology International QM 4 spectrofluorimeter with a BryteBox interface using FeliX32 software. Luminescence spectra were excited using a xenon short-arc lamp (USHIO, UXL-75XE) and recorded with a PTI detection system (model 814) and a photomultiplier tube (Hamamatsu, R928P) connected to a PTI lamp power supply (LPS-250B). Time-resolved spectra were excited with a xenon flash lamp (Hamamatsu, L4633) and recorded using a photomultiplier tube (Hamamatsu, R562) connected to a PTI XenoFlash power supply.

X-ray Data Collection. For complexes 2, 3, 4, and 7, the X-ray diffraction data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a Bruker AXS Apex II detector and a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å). Low temperatures were maintained using an Oxford Cryostream low temperature device. Data reduction was performed using the Rigaku Crystal Clear version 1.40.²⁹ Structures were solved by direct methods using SHELXT³⁰ and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.³¹ Structure analysis was aided by use of the programs PLATON³² and WinGX.³³ For complexes 5 and 6, the Xray diffraction data were collected at −173 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å). Low temperatures were maintained using an Oxford Cryosystems 700 lowtemperature device. Data reduction was performed using SAINT $V8.27B.^{34}$ The structure was solved by direct methods using SHELXT³⁰ and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.31 Structure analysis was aided by use of the programs PLATON³² and WinGX.³

DFT, Tolman Angle, and Percent Buried Volume (%V_B) Calculations. The program Firefly³⁵ was used for DFT calculations using the B3LYP functional with the following basis sets per atom: Sb, TZP; I, 6-311G; Cu, C, and H, 6-31G**. The ground state structure was geometry optimized from the X-ray coordinates, and the excited state triplet was, in turn, optimized from the ground state structure. The resulting structures were visualized with MacMolPlt.³⁶ The orbital energy diagram was constructed in Mathematica. Tolman cone angles were calculated using the Mathematica package FindConeAngle developed by Allen et al.³⁷ Percent buried volumes were calculated using SambVca (Cavallo et. al).⁴¹

RESULTS AND DISCUSSION

Synthesis and Rationale. Synthetic Novelty. We previously reported that several of the ligands used herein $(SbMe_2Ph, Sb^iPr_2Ph, and Sb^iPr_3)$ bind and structurally stabilize nickel(II).³⁸ In addition, several ligands employed in this work were previously synthesized by others $(SbCy_3, Sb^tBu_3, Sb^tBu_2Ph)^{39,40}$ or can be purchased commercially $(SbPh_3)$. While several of these ligands have been used in metalations with other 3d transition metals—both in our work and

others—only SbPh₃ has been used specifically in copper metalations; such studies only obtained monomeric and dimeric structures of CuX (X = Cl, Br, I),^{38,41-44} rather than the cuboid type structures of interest in this work. Thus, overall, with the stated exception of SbPh₃, none of the copperbinding parameters or structural motifs derived from homoleptic and heteroleptic SbR₃ ligands have been reported.

Electronic Ligand Effects. We targeted ligands sterically both larger and smaller than SbⁱPr₃, and with stronger and weaker donor strengths to investigate the full range of ligand effects on emission wavelength. Specifically, a previous study on electronic ligand effects in phosphine-supported thermochromic cuboids determined that while the ligand donor strength had the expected effect on the high-energy (HE, ³XLCT) emission (weaker ligand = lower energy emission), there was no correlation with low-energy (LE, ${}^{3}CC$) emission.⁴⁵ As only the LE band was observed in the single example of a published $Sb_4Cu_4I_4$ cuboid (1 derived from $Sb^{i}Pr_{3}$), we postulated that the primary effect of altering the organic substituents on the antimony donor atom would be steric rather than electronic. Additionally, the lack of access to a family of Sb₄Cu₄I₄ cuboids derived from para-substituted SbPh₃ derivatives (R = OMe, CH₃, H, CF₃)⁴⁵—due to the inability of SbPh₃ to support the cuboid motif-prevented the development of a classical Hammett relationship between donor strength and emission properties.

Second, the inclusion of a single phenyl unit in the ligand design would greatly amplify the breadth of synthetically accessible heteroleptic ligands with relative ease. In the pursuit of exclusively NIR emitters, we carefully considered whether a proposed series of SbR_2Ph ligands (R = alkyl) would impart the undesirable HE band observed in PPh3-based Cu4I4 cubes. For example, nearly all reported phenylphosphine-supported copper-halide cubes exhibit $LE \rightarrow HE$ thermochromism (high temp \rightarrow low temp) due to the $nb(I) \rightarrow \pi^*(Ph) XLMCT$.¹ However, deeper inspection of the literature reveals that the presence of two phenyl substituents (e.g., PPh₂Pr, PPh₂OEt, $PPh_2CH_2CH=CH_2$)^{17,46,47} is required to imbue thermochromism, whereas one phenyl unit is insufficient. For example, the PPhMeⁱPr supported cube is simply luminescent (LE emission only, $RT \rightarrow 77$ K).⁴⁸ Similarly, no detectable HE emission was observed in a Cu_4I_4 cluster without *any* aromatic substituent ($L = Pcyp_3$; cyp = cyclopentyl), but the cluster did exhibit thermoluminescence (like 1 derived from SbⁱPr₃).⁴⁹ Notably, there are several other examples of alkyl-only phosphorus-based cubes, but these were not investigated for their luminescent properties.^{50,51} Therefore, we confidently pursued the synthesis of several "monophenyl" substituted SbPhR₂ ligands with the premise of only steric consequences on LE emission.

Steric Ligand Effects. We hypothesized that as the steric bulk of the ligand decreased, the $\{Cu-SbR_3\}$ unit would be drawn closer to the cluster center due to fewer steric interactions with the neighboring SbR_3 ligands and the iodide ions. Consequently, we postulated smaller size would decrease the average Cu-Cu bond distance, thereby red-shifting the emission derived from the ³CC excited state in accordance with published trends.^{19,22,45,52} Although our work is exclusively performed with antimony ligands, these findings might apply to any copper-based luminescent clusters.

Synthetic Method of Ligands and Clusters. Antimony ligands with only one aryl group, such as SbMe₂Ph and SbEt₂Ph, have been synthesized previously, and others can be

synthesized by following a similar procedure.^{53,54} Each ligand was synthesized by reaction of the appropriate Grignard reagent with either SbCl₃ or SbCl₂Ph (crystallized to improve purity). The heteroleptic ligands (SbMe₂Ph, Sb[']Pr₂Ph, Sb[']Bu₂Ph) and Sb[']Bu₃ required distillations for purification, while the homoleptic ligands did not require additional purification. The copper metalation conditions in fluorobenzene (FPh) are similar to that previously reported for 1 (Sb[']Pr₃-based). However, the *tert*-butyl based clusters (**3** and **4**) precipitated from FPh, while cluster **2** proved insoluble in pentane during washing of the crude solid. A summary of the synthetic preparations of the ligands and metal complexes is depicted in Schemes 1 and 2, respectively.

Scheme 1. Synthetic Preparations of the Homoleptic and Heteroleptic Antimony Ligands

 $SbCl_{3} \xrightarrow{3 \text{ RMgCl}}_{Et_{2}O, \ \Delta \ 3 \ h} \xrightarrow{SbR_{3}}_{R = Cy, \ 'Bu}$ $\stackrel{2 \text{ SbCl}_{3}}{\xrightarrow{+}} \xrightarrow{PhSbCl_{2}} \xrightarrow{2 \text{ RMgX}}_{Et_{2}O, \ \Delta \ 3 \ h} \xrightarrow{PhSbR_{2}}_{R = Me, \ 'Pr, \ 'Bu}$ COMPROPORTIONATION

Scheme 2. Synthetic Preparations of the Copper-Antimony Cuboids and Dimers



X-ray Structures and Ligand Steric Effects. Dimeric Complexes. $Cu_2(I)_2(Sb^iPr_2Ph)_4$ (5), $Cu_2(I)_2(SbMe_2Ph)_4$ (6), and $Cu_2(I)_2(SbPh_3)_4$ (7). Following on our initial hypothesis that the steric size of the ligand dictates emission wavelength, we attempted to synthesize cuboids using smaller antimony ligands. Despite analogous reaction conditions to the synthesis of 1, this subset of antimony ligands bearing phenyl substituents provided dimers (Figure 1) rather than cuboid structures. The cone angles of the three ligands in this series $(SbMe_2Ph = 119^\circ < Sb^iPr_2Ph = 147^\circ < SbPh_3 = 155^\circ; Sb^iPr_3 =$ 155°; see next paragraph for discussion of the two 155° ligands) were calculated using the Cartesian coordinates from the crystal structures with the Mathematica program Exact Ligand Cone Angle.³⁷ Such small cone angles allow two ligands per copper atom, providing a dimer instead of a cuboid (cuboid = 1 SbR_3 ligand per copper). Thus, the evidence suggests that the cuboid motif can only be accessed with ligands that have a relatively large cone angle ($\sim \geq 155^{\circ}$).

Tolman Cone Angle vs Percent Buried Volume. An apparent discrepancy occurs when examining the calculated ligand cone angles for both $SbPh_3$ and Sb^iPr_3 . Both cone angles were calculated to be 155° , yet two $SbPh_3$ ligands were able to

coordinate in the case of 7, while only one SbⁱPr₃ ligand is bound per copper atom in cluster 1, implying that SbⁱPr₃ is sterically larger. This discrepancy can be rationalized by examining a different measure of ligand sterics, namely the percent buried volume (%V_B), a parameter that is regarded to more accurately define the steric bulk of a ligand.⁵⁵ The percent buried volumes of the four ligands were calculated using SambVca (Cavallo et. al),⁵⁶ affording the following values: SbMe₂Ph = 23.3% < SbPh₃ = 25.8% < SbⁱPr₂Ph = 26.0% < SbⁱPr₃ = 27.0% (Table 1). Thus, the %V_B values more accurately reflect the functional nature of the ligand sterics and compare favorably to the steric rankings of the analogous phosphine ligands.⁵⁷

The %V_B was equally accurate in predicting the propensity for larger ligands (cone angle ~ $\geq 155^{\circ}$; %V_B > 27.0%) to form the desired cuboid structures (see X-ray section, next paragraph); there were no exceptions. The traditional cone angle method provided the following values: SbCy₃, 152° < Sb'Pr₃, 155° < Sb'Bu₂Ph, 161° < Sb'Bu₃, 163°. [Note: our calculated ligand cone angles differ slightly from previously reported numbers (SbCy₃, Sb'Bu₂Ph = 166°; Sb'Bu₃ = 177°, Sb'Pr₃ = 157°)].⁵⁸ However, the %V_B calculations for these ligands provided a close match to the previously published cone angles. Overall, the clear %V_B cutoff between cube and dimer formation suggests that %V_B is the most reliable parameter.

Cuboid Structures. $Cu_4(I)_4(SbCy_3)_4$ (2), $Cu_4(I)_4(Sb^tBu_3)_4$ (3), and $Cu_4(I)_4(Sb^{t}Bu_2Ph)_4$ (4). The formation of dimers rather than cuboids from smaller antimony ligands prompted us to employ sterically bulkier antimony ligands. The crystal structures of the resulting antimony-supported copper-iodo cuboids 1-4 are depicted in Figure 2. At the core of each cuboid is a copper-based tetrahedron wherein the four copper atoms reside at the vertices. Each copper ion is bound to three iodine atoms, which in turn are each ligated in η_3 fashion to three copper ions. Each copper vertex is externally capped by an antimony ligand. The large steric bulk of the antimony ligand restricts the ligation of one (weak) antimony ligand per copper ion, which presumably drives the copper centers to assemble the cluster core. [Note: herein crystallographically unique bonds are presented in the conventional fashion; bond distance averages are stated in the format avg \pm s.d. for the n number of bond instances in the cluster. Cluster 2 ligated by SbCy₃ has an average Cu–Cu distance of 2.83 \pm 0.14. Å, an average Cu-Sb distance of 2.51 \pm 0.008 Å, and an average Cu–I bond distance of 2.68 \pm 0.02 Å. Despite being derived from a homoleptic ligand similar to 1, the tetrahedral core of 2 is not completely symmetric as found in the 4-fold symmetric Cu_4 core of $Cu_4(I)_4(Sb'Pr_3)_4$ (1, in cubic I23 space group), in which the unique crystallographic Cu-Cu bond length is 2.761(3) Å. In fact, each Cu-Cu distance in 2 is distinct from the other five Cu-Cu distances, with the shortest distance of 2.675(1) Å and the longest of 3.104(1) Å. In fact, the set of Cu-Cu distances for 2 represents (i) the broadest range of distances and (ii) both the shortest and the longest distances found in any cluster herein. Thus, these two extremes of high ligand symmetry and low crystallographic symmetry demonstrate that the selection of homoleptic ligand does not ensure access to a highly symmetric Cu₄ core in the solid state.

In fact, varying extents of Cu_4 core symmetry can be arbitrarily accessed with both homoleptic and heteroleptic antimony ligands. For example, the homoleptic ligand Sb^tBu₃ gives rise to the partially asymmetric Cu_4 core in



Figure 1. ORTEP diagrams (30% ellipsoids) for $Cu_2(I)_2(Sb'Pr_2Ph)_4$ (5) (top left), $Cu_2(I)_2(SbMe_2Ph)_4$ (6) (top right), and $Cu_2(I)_2(SbPh_3)_4$ (7) (bottom).

Table 1.	Average	Cu-Cu.	Cu-Sb.	and Cu-I	Bond	Distances	(Å)	for	Complexes	$1 - 7^{a}$
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	Cu-Cu _{avg}	Cu-Cu _{shortest}	Cu-Cu _{longest}	Cu-Sb _{avg}	Cu-I _{avg}	Cone Angle (θ)	$V_{\rm B}$
<u>Cuboids</u>							
$Cu_4(I)_4(Sb^iPr_3)_4$ (1)	2.761(3)	2.761(3)	2.761(3)	2.571(2)	2.707(2)	155	27.0
$Cu_4(I)_4(SbCy_3)_4$ (2)	2.83 ± 0.14	2.675(1)	3.104(1)	2.51 ± 0.008	2.68 ± 0.02	152	28.5
$Cu_4(I)_4(Sb^tBu_3)_4$ (3)	2.98 ± 0.03	2.9478(6)	3.0032(6)	2.55 ± 0.00004	2.69 ± 0.006	163	31.6
$Cu_4(I)_4(Sb^tBu_2Ph)_4$ (4)	2.82 ± 0.03	2.8037(7)	2.8618(8)	2.5381(5)	2.69 ± 0.01	161	29.9
Dimers							
$Cu_2(I)_2(Sb^iPr_2Ph)_4$ (5)	2.88 ± 0.03			2.54 ± 0.004	2.64 ± 0.01	147	26.0
Cu ₂ (I) ₂ (SbMe ₂ Ph) ₄ (6)	2.95 ± 0.04			2.53 ± 0.01	2.64 ± 0.02	119	23.3
$Cu_2(I)_2(SbPh_3)_4$ (7)	2.7255(5)			2.54 ± 0.007	2.63 ± 0.01	155	25.8
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"Also listed are the shortest and longest Cu–Cu bond distances for each complex, as well as the cone angle and percent buried volume parameter for each ligand.

 $Cu_4(I)_4(Sb^tBu_3)_4$ (3), which exhibits two sets (n = 3) of crystallographic Cu–Cu bonds at 2.9478(6) and 3.0032(6) Å. Relatedly, the cuboid derived from heteroleptic Sb^tBu_2Ph [$Cu_4(I)_4(Sb^tBu_2Ph)_4$, 4] also exhibits two sets of crystallographic Cu–Cu bonds at 2.8037(7) (n = 4) and 2.8618(8) Å (n = 2). It is notable that the differences in bond length between the shortest and longest Cu–Cu bonds in 3 and 4 are not nearly as exaggerated as in 2. All of these data reinforce the notion that ligand symmetry is not a (predictable) determinant of crystallographic cluster symmetry. All relevant bond distances for each of the three cuboids as well as $Cu_4(I)_4(Sb^tPr_3)_4$ are tabulated in Table 1.

The bond metric data indicates that irrespective of ligand choice, ligand symmetry, or crystallographic symmetry, there are only relatively small changes in the average Cu–Sb bond distances (2.51–2.57 Å) and virtually no change in Cu–I distances (2.68–2.71 Å). The Cu–Sb distances are typical for copper complexes with antimony ligands (~2.5 Å) and are understandably longer than the average distances of Cu–P (~2.25 Å) or Cu–As (~2.35 Å) bonds in the respective analogues.^{59,60} Lastly, the Cu–I bond distances are akin to any copper–pnictogen cuboid (~2.6–2.7 Å); there is no clear relationship between Cu–I distance and ligand design.^{45,50}

Luminescence. Each cuboid with Cu-Cu contacts was tested for its luminescent properties. The excitation and



Figure 2. ORTEP diagrams (30% ellipsoids) for $Cu_4(I)_4(Sb^iPr_3)_4$ (1, previously reported, top left),²² $Cu_4(I)_4(SbCy_3)_4$ (2, top right), $Cu_4(I)_4(Sb^iBu_3)_4$ (3, bottom left), and $Cu_4(I)_4(Sb^iBu_2Ph)_4$ (4, bottom right).

emission profiles of four cuboids (1-4) at 77 K are depicted in Figure 3 (1: SbⁱPr₃; 2: SbCy₃; 3: Sb^tBu₃; 4: Sb^tBu₂Ph). Compared with phosphine-supported copper cubes at 77 K, only a single emission is observed for 1-4—analogous to the low-energy (LE) band typically exhibited in the 500–600 nm region for P₄Cu₄I₄ cubes. Notably absent from the emission spectra of 1-4 is the characteristic high energy (HE) band found in thermochromic phosphine-supported cubes, which is



Figure 3. Excitation and emission maxima for complexes 1-4 at 77 K.

generally observed in the 400-500 nm range. At the first approximation, the lack of the HE band in 1-4 can be attributed to the lack of phenyl groups as antimony substituents (i.e, the phenyl-based $nb(I) \rightarrow (\pi^*)$ Ph XLCT triplet state is obviated). The single exception to this is cluster 4 (derived from Sb^tBu₂Ph); however, previous work using a single-phenyl phosphine (namely, PPhⁱPrMe) also did not display the HE band, suggesting that multiple aryl units are required to activate the XLCT pathway, as explained and hypothesized in the Electronic Ligand Effects subsection. Overall, considering the excitation profiles of the colorless samples of 1–4 ($\lambda_{ex} \approx 350$; similar to phosphine cubes), this results in a very large Stokes shift of ~250 nm. Modulation of the λ_{ex} did not result in any noticeable change in the emission profiles of 1-4; namely, the appearance of the HE band was never observed.

However, the room temperature emission spectra of 1–4 do not exhibit any appreciable luminescence compared with the low temperature spectra (Figure S11). This is in stark contrast to the ambient temperature emission from phosphinesupported cubes, in which a dominant LE band (500–600 nm) is preserved. An illustrative comparison is the case of $[Cu_4(I)_4(PPh^iPrMe)_4]$, a phosphine-supported cube reported by Harvey (with no XLCT) that exhibits *room temperature* luminescence at 580 nm (LE band);⁴⁸ the phenyl-free cluster $[Cu_4(I)_4(Pcpent_3)_4]$ reported by Perruchas exhibits similar properties ($\lambda_{em} \approx 520$ nm).⁴⁹ Such emission can be attributed exclusively to the cluster-centered (³CC) emission mechanism.



Figure 4. Variable temperature (153-222 K) luminescence of clusters 2 and 4.

By comparison, our cluster 2 exhibits a similar (intermediate) emission energy ($\lambda_{\rm em} \approx$ 560 nm) and yet does not emit at room temperature. Thus, the room temperature quenching of emission in 1-4 cannot exclusively be due to the red-shifted emission profiles. Although it can be postulated that lower energy emissive states generally have shorter lifetimes due to increased probability of nonradiative decay pathways,^{61,62} it is clear in this case that the precise identity (P vs Sb) and coordinates (long vs short bonds, vide infra) of atoms in this family of clusters is critical in determining the accessible photoactive states. On a similar note, these clusters are nonemissive in the solution state at room temperature, likely due to the aforementioned nonradiative decay pathways. Further supporting the "suppression of nonradiative decay" hypothesis, at low temperatures both pentane and 2-MeTHF solutions of the clusters remain emissive.

To clearly showcase the precise temperature dependence and the lack of multiple emissions at other temperatures, variable temperature luminescence measurements were collected. The variable temperature fluorimetry data for clusters 2 and 4 are depicted in Figure 4. The luminescent LE bands for 2 and 4 are quite prominent at -120 °C (liq N₂/ pentane bath; 153 K), but for each cluster the luminescence intensity decreases to baseline as the temperature increases to 298 K. There is a slight shift in the λ_{em} of **2** from 661 nm (low temp) to 681 nm (RT), whereas a negligible λ_{em} shift occurs for cluster 4 in the same temperature regime. The emission from both 2 and 4 becomes essentially nonemissive above 230 K. The small shift in λ_{em} for 2 (20 nm) is interesting but not indicative of the authentic dual emission found in thermochromic systems. Such small shifts in λ_{em} (< ~50 nm) have been observed in many cuboids and have been postulated to originate from symmetry distortions inside the Cu₄ core.^{63–65} Intriguingly, the structural data for 4 reveal some extent of homogeneity among its Cu–Cu bond distances (4×2.80 Å; 2 \times 2.86 Å), while cluster 2 exhibits six unique bond lengths one for every Cu-Cu interaction. Similarly, the originally reported cluster 1-which exhibits complete homogeneity of Cu-Cu contacts: 6 × 2.76 Å-also did not exhibit any significant shift in λ_{em} across variable temperatures.²² Thus, our data is consistent with the previously asserted connection between cluster symmetry and a small, temperature dependent wavelength shift in the LE emission.^{63–65}

Cluster 3 was also tested for its luminescent properties, wherein it exhibited a similar extent of luminescence to 2 and 4 at 77 K. However, variable temperature measurements under the same conditions as those used for 2 and 4 at -120 °C (liq N₂/pentane bath; 153 K) revealed a greatly diminished intensity compared with the 77 K measurement. Thus, another temperature bath regime was used at -152 °C (liq N₂/ isopentane; 121 K) to obtain the thermal decay of emission intensity (Figure 5). The emission feature in the resulting data



Figure 5. Variable temperature (123–233 K) luminescence of cluster 3.

for 3 rapidly declines as a function of increasing temperature, and the emission intensity when warmed from -152 to -120 °C is approximately 25% of the emission intensities from 2 and 4 at the same temperature.

Structure–Luminescence Correlations. *Temperature Dependent Structures and Emission.* The marked difference of 3 in its diminished luminescence intensity (from 1, 2, and 4) motivates the exploration of any possible correlation between structural parameters and luminescence properties. Out of all of the clusters studied herein, cluster 3 is most notable in that it exhibits the longest average Cu–Cu distances (2.98 Å) by a wide margin—significantly longer than the next closest Cu–



Figure 6. For cuboids 1 (*left*) and 3 (*right*), correlation between the temperature dependent changes in X-ray structure (Cu–Cu, Cu–Sb, or Cu–I bond distances) and percent of maximum luminescence intensity (red data points).

Table 2. Table of L	igand Cone Angles,	Average Cu-Cu Bo	nd Distances, Emission	n Wavelengths, and	d Other Pe	rtinent Bon	d
Distances for Comp	olexes 1–4						

	$Cu_4(I)_4(Sb^iPr_3)_4$ (1)	$Cu_4(I)_4(SbCy_3)_4$ (2)	$Cu_4(I)_4(Sb^tBu_2Ph)_4$ (4)	$Cu_4(I)_4(Sb^tBu_3)_4$ (3)
%V _B	27.0	28.5	29.9	31.6
Emission (λ)	711	666	575	558
Cu–Cu avg (Å)	2.761	2.826	2.822	2.975
Shortest Cu-Cu	2.761	2.679	2.803	2.997
Longest Cu-Cu	2.761	3.097	2.861	3.003
# of unique (crystallographic) Cu–Cu bonds	1	6	2	2

Cu_{avg} value (2.83 Å, for **2**). Previously, it was suggested that 2 × the van der Waals radius of copper (2.80 Å) was the theoretical cutoff for copper-centered LE emission, as beyond that distance cuprophilic interactions cease.^{65,66} However, that has been disproven in the case of phosphine-supported cubes, wherein LE emission ($\lambda_{em} = 500 \text{ nm}$) has been observed up to Cu–Cu_{avg} = 3.47 Å, as in the case of [Cu₄(I)₄(tmp)₄]—where tmp = tris(3-methylphenyl)phosphine.⁶⁷

In the previous communication, crystal structures of 1 (derived from SbⁱPr₃) solved across a range of temperatures (100–300 K) established a correlation between Cu–Cu bond length and emission intensity; for clarity, an updated version of this plot is presented herein as Figure 6 (*left*). It was notable for 1 that the only significant changes in bond distances from 100 to 300 K occurred in the Cu–Cu contacts, and the Cu–I and Cu–Sb bond lengths remained relatively invariant. Due to the vastly different temperature profile of 3 (temperature of emission "turn-on", $T_{\rm em} = 100-125$ K) compared with the other cuboids (1, 2, and 4: $T_{\rm em} \approx 200$ K), we determined the structure–luminescence correlation for 3 using the same variable temperature X-ray structure method (Figure 6, *right*).

Regarding the temperature dependent X-ray structure metrics, the same general trends are observed for 3 as for 1. The Cu–I and Cu–Sb bonds remain relatively constant across the 200 K range. As cluster 3 possesses two sets of crystallographic Cu–Cu distances, each individual data set is plotted (gray) as well as the average distances and trendline (black). Notably, the change in Cu–Cu distances for 3 across the temperature range is 0.08 Å, nearly identical to that for 1.

However, all of the Cu-Cu distances found in 3 are longer than those for 1 irrespective of any temperature considerations. Regarding the emission, it is important to note that both 1 and 3 exhibit comparably strong luminescence at 77 K, but they exhibit different characteristic "turn-on" temperatures (T_{em}) upon cooling. The T_{em} was collected by determining the ratio of the luminescence intensity at varying temperatures (collected during the variable temperature luminescence measurements) to the intensity at 77 K, affording a parameter defined as "percent max intensity". A full graphical representation of each cuboid's percent max intensity at varying temperatures along with a more detailed explanation of the process to determine this parameter can be found in Figure S12. Despite the very low temperature used in a controlled cooling bath (isopentane/liq N₂; 123 K), cluster 3 remains weakly emissive compared with 1 at an even higher temperature (pentane/liq N₂; 163 K). As a result, the exact emission "turn-on" temperature remains elusive for 3 but is likely in the 100-125 K range, which is correlated with Cu- $Cu_{avg} \approx 2.96$ Å. It is thus evident that the 2.80 Å van der Waals "cutoff" is not a litmus test indicator for luminescence, but instead there is a correlation between the $\mathrm{Cu-Cu}_{\mathrm{avg}}$ and characteristic T_{em} value (shorter Cu-Cu_{avg} = higher T_{em}).

Effect of Phenyl Substituents on Thermochromism versus Thermoluminescence. Complexes 1, 2, and 3 lack any aromatic character in the ligand backbone, which has been proven necessary to observe the competing ${}^{3}CC \leftrightarrow {}^{3}XLCT$ -(aryl) emissions that are present in dual-emitting thermochromic compounds (a more detailed explanation can be found in



Figure 7. Graphical summary plot of emission wavelength versus percent buried volume.

previous sections). Therefore, purely thermoluminescent properties are expected and, indeed, observed. Regarding cluster 4 ($L = Sb^tBu_2Ph$), the temperature dependent emission (Figure 4) clearly exhibits a single emission feature at all temperatures, consistent with the expectation of thermoluminescence only. Thus, from the combination of low temperature and variable temperature luminescence studies, it appears that the "two-phenyl" rule for thermochromism remains constant from phosphine to stibine systems. However, we do note that the possible counter-example of an SbPh₂R-supported cuboid has remained synthetically inaccessible at present.

Correlation between Steric Bulk and Emission Energy. A correlation is evident between the steric size of the ligand and the maximum emission wavelength (Table 2, Figure 7). Of all cuboids 1-4, the lowest-energy emitting cuboid is the original complex, $Cu_4(I)_4(Sb'Pr_3)_4$ (1), with $\lambda_{em} = 711$ nm, which also exhibits the lowest %V_B at 27.0%. As tabulated in Table 2 and illustrated in Figure 7, for clusters 1-4 an increasing %V_B is correlated with decreasing λ_{em} values vis a vis blue-shifted emission energies. The cuboids synthesized with SbCy₃ (%V_{bur} = 28.5%), Sb^tBu₂Ph (%V_{bur} = 29.9%), and Sb^tBu₃ (%V_B = 31.6%) have emission wavelengths of 661, 575, and 558 nm, respectively. This trend is also structurally correlated to the average Cu-Cu bond distances in the cluster, wherein sterically smaller ligands result in shorter Cu-Cu_{ave} distances (lower emission energies). The correlation between smaller ligands and shorter $Cu-Cu_{avg}$ distances likely arises because the entire { $Cu-SbR_3$ } unit is best able to approach the center of the cluster when $\{Cu-SbR_3\}$ is small. Notably, the overall importance of steric effects in this series of copper dimers/ clusters is evident in that any ligands smaller than Sb'Pr₂Ph resulted in exclusive dimer formation (which accommodates cis SbR₃ ligands) rather than forming tetramers (SbR₃ is too big for the *cis* motif).

An interesting caveat to this data resides in the comparison of cluster 2 with cluster 4: these clusters exhibit nearly identical Cu–Cu_{avg} distances $(2.826 \pm 0.14 \text{ and } 2.822 \pm 0.03 \text{ Å},$

respectively) and yet exhibit a 100 nm difference in emission wavelength (666 and 575 nm, respectively). This implies the existence of another subtle structural reason for the vast difference in emission energy. As Perruchas has demonstrated that ligand donor strengths in phosphine-based cubes have no trend-wise effect on LE emission,45 we postulate that the explanation can again be found in the structural metrics. Closer inspection reveals that 2 exhibits the shortest Cu-Cu bond (2.679 Å) found in *any* of the clusters. In contrast, the shortest Cu-Cu bond in 4 resides at 2.803 Å. DFT calculations reveal that the LUMO in the ³CC transition is due to an MO that is highly delocalized across the cluster center, as opposed to an individual lowest lying molecular orbital.^{68,69} While it has been shown that short Cu-Cu bond distances do red-shift the emission, it is not clear whether the presence of a few particularly short Cu-Cu bonds in a cluster center will similarly adjust the maximum emission wavelength in these complexes.^{70,71} However, there is some precedent for this phenomenon.^{64,65,71–73} Kim et. al synthesized two crystallographic isoforms of the same cubane (derived from 2-(cyclohexylthio)-1-thiomorpholinoethanone) that differed in their solvation state (desolvated versus MeCN solvate). The two structures had similar $\rm Cu-Cu_{avg}$ distances (2.70 vs 2.71 Å), but the range of Cu-Cu bond lengths within the cluster ranged from 2.607-2.773 Å for the desolvated cluster versus 2.643-2.771 Å for the CH₃CN solvated cluster. The presence of the shorter Cu-Cu bond distance in the desolvated structure resulted in a red-shifted $\lambda_{\rm em}$ = 600 nm, compared with the 540 nm emission of the cluster with the longer shortest Cu-Cu distance.⁷¹ Similar results were reported in two other cases, where although the two comparative compounds displayed $Cu-Cu_{avg}$ bond distances separated by less than 0.02 Å, one compound contained a significantly shorter Cu-Cu_{min} bond distance. In each case, the compound with the shorter Cu-Cu_{min} distance had a red-shifted λ_{em} by 40–50 nm.^{73,74} Overall, these examples plus the work described herein (notably, 2 and 4) suggest that the average Cu-Cu distance



Figure 8. (*Left*) Excitation and emission features (77 K) for cluster 8 showing $\lambda_{em} = 670$ nm; (*right*) Variable temperature luminescence (143 to 253 K) for 8.

provides a first approximation rank-order correlation between structure and emission wavelength (shorter distance = red-shifted λ_{em}). However, when similar Cu-Cu_{avg} values are present, the shortest Cu-Cu_{min} results in the more red-shifted emission profile.

Correlation between Crystallographic Symmetry and Emission Energy. Based on the metrics discussed above showing that clusters supported by the smallest SbR₃ ligand resulted in the most red-shifted NIR emission, we synthesized the next smallest ligand in the series-namely SbⁱPr₂Ph. Indeed, this intermediate-sized SbR₃ ligand was the only case where we isolated both a dimer (5) and tetranuclear cluster (8) by varying the ligand equivalents (excess versus 1:1, respectively). This suggests that the $%V_B$ of Sb'Pr₂Ph (26.0%) is of truly intermediate steric bulk between the small set $[\%V_B]$ $\leq 25.8\%$ (SbPh₃)] and large set $[\%V_B \geq 27.0\%$ (SbⁱPr₃)] of antimony ligands. Another (unintended) difference was the lower symmetry of SbⁱPr₂Ph versus SbⁱPr₃. Unfortunately, due to competing space groups of crystallization, the exact structure of the SbⁱPr₂Ph cuboid 8 could not be precisely determined, although several partial structure solutions unambiguously support an asymmetric cuboidal structure and Cu-Cu bond lengths in the 2.7-2.8 Å range and on average are about equal to the 2.76 Å Cu–Cu bond distance in 1. A collection of ball-and-stick representations of the Sb₄Cu₄I₄ core of 8 are provided in Figure S13. Presumably as a result of the lower symmetry of Sb'Pr₂Ph versus Sb'Pr₃, the partial structures can be solved in triclinic, tetragonal, or rhombohedral space groups—but all of these are of lower symmetry than that of SbⁱPr₃ supported 1 (cubic, I23). As a corollary, while 1 exhibits just a single crystallographically unique Cu-Cu bond, the partial structures of 8 reveal the following sets of unique Cu-Cu bonds: six sets of 1 (triclinic), two sets of 3 (rhombohedral), or one set of 2 plus one set of 4 (tetragonal).

The luminescence properties of this cuboid (Figure 8) reveal several intriguing insights. First, while 8 emits in the red-shifted region (670 nm) in this series (558–711 nm), cluster 1 still emits 40 nm further into the NIR. Additionally, 8 is the only cluster that is quantitatively emissive at room temperature, as evidenced by the VT and $T_{\rm em}$ emission profiles seen in Figure 8 and Figure S12. Additionally, lower temperatures blue-shifted the emission energy by ~15 nm, which can be attributed to the symmetry-imposed distortions in the Cu core,

as explained previously in the case of complex 2 (vide supra the Luminescence section and Figure 4). The average nominal Cu–Cu bond distance in 8 is roughly ~2.7 Å, which would imply the emission of this complex to be similar to 1 if the emission was derived purely from the length of the Cu–Cu bonds in the cluster center. Overall, 8 clearly follows the λ_{em} trend established by the ligand sterics and Cu–Cu bond lengths found in 2, 3, and 4. Indeed, the result of this analysis firmly places 1 as the outlier in the series. Notably, 1 is the only cubic structure in the series with just a single crystallographically unique Cu–Cu bond.

A relationship between the LE emission and crystal symmetry was first suggested by Hardt and Pierre, who noticed the presence of a 4-fold symmetry element led to redshifting of emissions.⁶³ Later, Holt and co-workers synthesized several luminescent clusters with general structure $Cu_4(I)_4(CH_3CN)_2(L)_2$ (L = aniline derivative). One complex with L = 2,6-dimethylaniline had no internal symmetry element, a Cu-Cu_{avg} bond distance of 2.706 Å, and λ_{em} = 568 nm. Another complex with L = p-anisidine had $Cu-Cu_{ave}$ = 2.716 Å but did contain an internal 2-fold symmetry element. The latter cluster displayed an emission of 608 nm, significantly red-shifted as compared to the lower symmetry compound.⁶⁵ In a separate instance, two polymorphs of the luminescent cluster, Cu₄(I)₄(PPh₂OEt)₄, were synthesizedone with tetragonal symmetry and the other monoclininc. Although the Cu-Cu_{avg} bond distances for the two were drastically different (3.056 Å for tetragonal, 2.871 Å for monoclinic), the two compounds displayed remarkably similar emission profiles for the LE emission ($\lambda_{em} = 570$ and 580 nm for the tetragonal and monoclinic structures, respectively).⁴⁶ These examples, along with our current findings, provide further evidence for the correlation between symmetry and $\lambda_{\rm max}$ for the LE emission.

Correlation between Electronic Ligand Effects and Emission Energy. Recently, Perruchas et al. determined there was no discernible correlation between the electronic properties of the ligand and the energy of emission originating from the cluster center (³CC).⁴⁵ Our results corroborate those findings. Using the classical Tolman electronic parameter (TEP) to define the electronic strength of our antimony ligands, we have shown previously that the addition of a single

phenyl group does lower the TEP versus an all-alkyl analogue, while higher aliphatic organic substituents increased the TEP (i.e., isopropyl versus methyl).³⁸ Although it is difficult to quantify the TEP for the bulkier ligands (e.g., Sb^tBu3, SbCy₃), we can extract useful information by examining analogous phosphine compounds ($P^{t}Bu_{3TEP} = 2056 \text{ cm}^{-1}$; $PCy_{3TEP} =$ 2056 cm⁻¹).⁷⁵ Thus, an approximate order of Sb-ligand strength would follow as $Sb^{t}Bu_{3} = SbCy_{3} > Sb^{t}Bu_{2}Ph > Sb^{i}Pr_{3}$ > SbⁱPr₂Ph. If electronic effects were crucial in determining the ³CC λ_{em} , it would be expected that the emission energies follow this trend as well. However, the emission energies do not, in fact, follow this trend, as the emission for complex 1 is further red-shifted versus complex 8 and similarly for complexes 2 and 3. Although from both our results and those of Perruchas, there does appear to be a trend between increasing electron withdrawing ligand effects and decreasing Cu–Cu bond lengths, there does not appear to be a definitive correlation between said effects and the emission energy originating in the Cu-Cu core.

Lastly, lifetime measurements were collected for all of the clusters and are tabulated in Table 3. Based on the relatively

Table 3. Lifetime Measurements for Clusters 1-4 and 8 at Low Temperature and Room Temperature

Cluster	77 K λ _{ex} (nm)	77 K λ_{em} (nm)	77 K τ (μs)	298 K τ (μs)
$Cu_4(I)_4(Sb^iPr_3)_4$ (1)	380	711	7.7 ± 0.4	1.2 ± 0.09
$\begin{array}{c} Cu_4(I)_4(Sb^iPr_2Ph)_4\\(8)\end{array}$	369	670	7.7 ± 0.05	0.36 ± 0.05
$Cu_4(I)_4(SbCy_3)_4$ (2)	355	666	9.8 ± 0.05	0.43 ± 0.04
$\begin{array}{c} \operatorname{Cu}_4(I)_4(\operatorname{Sb}^t\operatorname{Bu}_2\operatorname{Ph})_4\\(4)\end{array}$	341	575	5.4 ± 0.8	0.42 ± 0.06
$Cu_4(I)_4(Sb^tBu_3)_4$ (3)	339	558	5.9 ± 0.03	0.39 ± 0.05

long microsecond lifetime in each case in a narrow range $(5.4-9.8 \ \mu s)$, it is clear that all of the clusters undergo the same phosphorescence-based emission process. At room temperature, the lifetimes decrease by an order of magnitude. No apparent trend is evident between the ligands, complexes, or emission wavelengths and the lifetimes. However, the stark difference between the room temperature and low temperature lifetimes partially explains the lack of luminescence at room temperature. Additionally, the nonradiative decay pathways are mitigated as the temperature is lowered, thus accessing the phosphorescent emissions with longer lifetimes.

Density Functional Theory (DFT) Calculations for 1. DFT calculations undertaken on the ground state singlet (based on X-ray structure) and excited state triplet (geometry optimized S = 1 state) describe the electronic states available in the luminescent copper cuboids, and they have been performed and reported.^{68,69} The calculations performed on one of the first thermochromic compounds, $[Cu_4(I)_4(pyridine)_4]$ cluster, elucidated the origins of the lower energy XLCT excited state and the higher energy CC excited state and determined that the pyridine π^* orbitals were the LUMO responsible for the XLCT transition. Although this is consistent with the lack of a second emission band in our first thermoluminescent compound (1), a full DFT study on the singlet and triplet states of that and related compounds is critical to understand the origins of the copper-antimony cuboid luminescence. Thus, DFT calculations were performed on the singlet and triplet states of 1. The geometries for both

the ground and excited state were optimized using the B3LYP functional with the following basis sets per atom: Sb, TZP; I, 6-311G; Cu, C, and H, 6-31G**. The calculations were performed without any symmetry impositions.

Figure 9 depicts the ensemble of MOs resulting from the S_0 (*left*) and T_1 optimized geometries; both the α and β spin manifolds of T_1 are represented (middle and right, respectively). From the MO diagram of the ground state (S_0) , the HOMO consists primarily of the Cu 3d-orbitals with a small contribution from the iodine 5p orbitals. At slightly lower energy, the occupied MOs are a cluster of orbitals resulting from various admixtures of the Cu and I orbitals, with small contributions from the Sb 5p set. The LUMO of the ground state (S₀) consists almost entirely of Cu-Cu bonding character (4s) with an incredibly symmetric profile, with a small extent of I parentage (5p). This highly symmetric orbital was labeled A_1 to reflect that property. The lack of any contribution from the antimony R groups provides insight for the lack of the HE band (XLCT, ligand-based) in the emission profile. The next higher energy group of unoccupied MOs resides on the antimony atoms, with some extension onto the isopropyl carbons. These data suggest that a second (HE) emission band may be possible provided the presence of more aromatic character on ligand. However, from the previous discussion, we have determined it would require multiple (≥ 2) aryl substituents to decrease the energies of those orbitals to a level competitive with the copper-based emission.

The T_1 state of 1 was geometry optimized in the S = 1configuration. Obtaining this geometry optimized structure required a slow progression at low basis set levels away from the S₀ geometry, followed by higher level calculations that converged on the final calculated structure for the T1 state. The conversion from ground state singlet to excited state triplet often enacts large geometric distortions, especially among the Cu-Cu and Cu-I bond lengths.^{68,69} The relevant bond distance data are tabulated in Table 4, along with the experimental distances acquired from the crystal structure. The most notable difference between the DFT calculated ground state for 1 and the X-ray structure of 1 is the discrepancies in Cu-Cu bond lengths [DFT: 2.424 ± 0.004 ; X-ray: 2.761(3)]. This highlights the fact that the Cu₄ core is especially elastic with respect to temperature, considering the temperature of Xray data collection (100 K) versus the "temperature" of DFT calculation (0 K). Upon conversion from S_0 to T_1 , the excited state exhibits contracted Cu–Cu contacts $(2.36 \pm 0.04 \text{ versus})$ 2.424 \pm 0.004), and expanded Cu-I bonds (3.09 \pm 0.29 versus 2.839 \pm 0.007) that compensate for the contracted Cu₄ core. There is little change in the Cu-Sb bond lengths between ground and excited states, which is common even among Cu-P based cubes.¹⁹ Overall, it is clear from both the calculated and experimental data that the origin of luminescence for all the Cu-Sb clusters presented herein is centered inside the cluster.

Most Importantly, the Highest SOMO Consists of an Incredibly Symmetric and Delocalized Set of Cu 3d Orbitals, with Minor Contributions from the lodine 5p Orbitals. The highest SOMO of T_1 exhibits decreased energy relative to the S_0 LUMO by nearly 2.5 eV (both denoted with the A_1 symmetry label, reflecting the similar origins from the Cu₄ core). This phenomenon of energy stabilization of the Cu–Cu electron density responsible for the CC excited state between ground and excited states has been observed in calculations on the analogous pyridine supported cube, with a similar degree of



Figure 9. Molecular orbital diagram of 1 showing the ground and excited states, along with selected orbital parentage images.

Table 4. Relevant Bond Distances for the Calculated Singlet and Triplet States, and the Associated Experimental (X-ray) Bond Distances for 1

	Cu-Cu	Cu–I	Cu-Sb
S_0 (DFT)	2.424 ± 0.004	2.839 ± 0.007	2.544 ± 0.002
T_1 (DFT)	2.36 ± 0.04	3.09 ± 0.29	2.52 ± 0.02
Experimental (X- ray)	2.761(3)	2.707(2)	2.571(2)

energy stabilization in the pyridine case ($\sim 2.5 \text{ eV}$).⁶⁹ For the pyridine cube, the stabilization lowers the energies of these orbitals past the π^* orbitals of the pyridine ring, which are the original LUMOs in the ground state and the LUMOs for the second (HE) transition (X/MLCT). In contrast, our system exhibits orbital properties similar to other cubes without phenyl substituents, and the calculated MO diagram appears similar, too.⁴⁹ These systems display a unique single low-lying triplet state, and it is clear that occupation of only one triplet state is plausible. The LUMO of the T_1 excited state in 1 (the excited state of the excited state) displays significant Sb character, with an additional large amount of electron density located along the Cu-I core. The LUMO+4 is comprised primarily of Sb 4p orbitals with some additional interaction with the Cu 3d orbitals, which interestingly is very similar to the LUMO+1 cluster of orbitals in the ground state. The previous HOMO of the ground state, consisting of Cu (3d) and I (5p) parentage, is the new HOMO-2 cluster in the

the S_0 HOMO and the highest energy SOMO of T_1 represents the energy of the phosphorescent emission from the LE band that is experimentally observed. The corresponding calculated emission wavelength was determined to be 1604 nm, which is quite red-shifted from the experimental value (711 nm). Such a deviation from experimental spectroscopic energies is not uncommon in DFT calculations on multinuclear transition metal complexes, in general,⁷⁶ and for B3LYP in particular.⁵⁹

triplet excited state, showcasing the consistency between the

two calculations for cluster 1. The energy difference between

In conclusion, the two critical orbitals involved in the $S_1 \rightarrow T_1$ intersystem crossing process—as well as the $T_1 \rightarrow S_0$ emission process—are highly symmetric, Cu(3d)-based MOs whose delocalization and resultant energy are dependent on the symmetry of the cluster. Such interpretation of the DFT calculations is consistent with the experimental observation that the cluster with the highest symmetry (1) allows for the population of the most symmetric and lowest energy MOs in a Cu₄I₄Sb₄ system. We conclude that the extremely high crystallographic symmetry of 1—in conjunction with the small %V_B of SbⁱPr₃ and corresponding short Cu–Cu_{avg} bond distances—results in cluster 1 exhibiting the lowest energy NIR emission (711 nm) in this series of clusters. This work convincingly relays that future designs for NIR emissive Cu₄ clusters must obtain shorter Cu–Cu bonds while retaining the

Inorganic Chemistry

highest possible (cubic) crystallographic symmetry—likely via the clever design of smaller, cuboid-supporting homoleptic ligands derived from antimony or other main group elements.

Several additional and important trends and conclusions can be explicitly listed as follows:

- (1) Similar to other work on copper cubes, we find that cubes derived from ligands with 0 or 1 phenyl unit(s) do not exhibit thermochromism; rather, only thermoluminescence is observed.
- (2) Antimony ligands with large R groups (${}^{i}Pr_{3}$, ${}^{t}Bu_{3}$, ${}^{t}Bu_{2}Ph$, Cy₃) exclusively provide cuboid structures. In contrast, smaller R groups (Ph₃, Me₂Ph) provide dimeric species (not luminescent). Ligands with intermediately sized R-groups (${}^{i}Pr_{2}Ph$) can access both structural motifs.
- (3) Regarding ligand sterics, percent buried volume ($^{\%}V_B$) is superior to the conventional Tolman cone angle metric in terms of accurately reflecting the functional size of ligands that support cuboids (large) versus dimers (small).
- (4) The combination of short Cu–Cu bond and a Cu_4 core possessing highest crystallographic symmetries is required for NIR emission.
- (5) Among cubes with similar average Cu–Cu bonds, the presence of a *single* short Cu–Cu bond red-shifts the λ_{em} value.
- (6) Lastly, shorter average Cu–Cu bonds (regardless of symmetry) lead to higher $T_{\rm em}$ values—that is, luminescence occurs at temperatures closer to ambient conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00229.

NMR spectra of ligands and metal complexes; X-ray diffraction details; crystallographic data and refinement parameters of complexes 2-7; additional luminescence figures; ball and stick models for the partial structure of 8; percent of max intensity vs temperature curves for complexes 1-4 and 8 (PDF)

Accession Codes

CCDC 1882285–1882290 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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