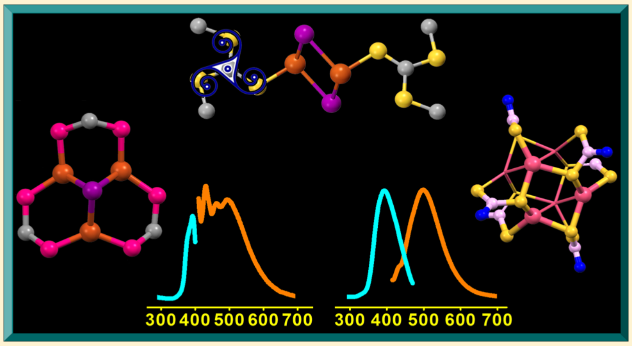
Inorganic Chemistry
Article
pubs.acs.org/IC

Impact of Ligand Framework on the Crystal Structures and Luminescent Properties of Cu(I) and Ag(I) Clusters and a Coordination Polymer Derived from Thiolate/Iodide/dppm Ligands

Gunjan Rajput,[†] Manoj Kumar Yadav,[†] Michael G. B. Drew,[‡] and Nanhai Singh*,[†]

[†]Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India
[‡]Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, U.K.

Supporting Information



ABSTRACT: New homoleptic hexanuclear Ag(I) and heteroleptic trinuclear Cu(I) clusters and a Cu(I) coordination polymer (CP) of the formulas [Ag$_6$(dtc)$_6$] **1**, [Cu$_3$I$_2$(dppm)$_3$(dtc)] **2**, and [Cu(ttc)I]$_\infty$ **3** (dtc = *N*-methylbenzyl-*N*-methyl-thiophenedithiocarbamate; dppm = 1,1-bis(diphenylphosphino)methane; and ttc = dimethyltrithiocarbonate) were synthesized and characterized by elemental analysis, IR, UV−vis, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, and their structures were elucidated by X-ray crystallography. The complexes show interesting structures and luminescent properties. Complex **1**, which is centrosymmetric, contains four short Ag···Ag interactions at 2 × 2.966(1) and 2 × 3.014(1) Å. There are also several Ag···Ag distances of 3.3−3.4 Å. The molecule shows hexagonal orientation with alternating silver and sulfur atoms of the overlapping Ag$_3$S$_3$ hexagons in the front and rear, along the *a* axis. Complex **2** is a rare trinuclear cluster complex of Cu(I); the Cu···Cu distances are 2.906(2), 3.551(2), and 3.338(2) Å, the foremost representing a substantial intermetallic contact. The Cu$_3$I$_2$P$_6$S$_2$ core is comprised of three fused distorted hexagonal rings with the I1 atom located at the center participating in all three rings. Complex **3** is an iodide-bridged CP with a "staircase"-like arrangement in which the Cu(I) is tetrahedrally surrounded by a sulfur atom from the ttc ligand and three iodine atoms. Unlike **3**, which is nonluminescent, **1** and **2** are strongly luminescent in the solid and solution at room temperature. The time-resolved emission spectra reveal a triexponential decay curve and short mean lifetime characteristic of fluorescence behavior. Diffuse reflectance spectroscopy revealed semiconducting behavior with band gaps of 2.12, 3.01, and 2.18 eV for **1**−**3**, respectively.

■ INTRODUCTION

Current interest in the design and synthesis of mono- and multinuclear complexes and clusters with closed-shell d^{10} metals (Cu, Ag, Au) stems from their structural diversity, intriguing luminescent properties, and applications as sensors, nanomaterials, sensitizers in solar energy conversion processes, biological imaging agents, and OLED materials.[1,2] Also, Cu(I) sulfur-bridged complexes with thiolate or sulfide ligands have been found to play a crucial role in some metalloproteins in biological systems.[2h,i] The metallophilic interactions observed in these compounds play an important role in their photoluminescent properties.[1−4] In comparison to Ag(I), the luminescent Cu(I) and Au(I) clusters and polymeric complexes have been extensively studied because of the high photosensitivity of the former.[5] Furthermore, the rich structural features and utilitarian considerations have been the main driving force behind the synthesis of Cu(I) and Ag(I) clusters and coordination polymers with different donor ligands.[1−4] Much attention has been devoted in recent years to the synthesis and luminescent properties of Cu(I) clusters and multinuclear complexes in which the coordination sphere of the metal is closely controlled through the use of bulky chelating and monodentate ligands. The best developed systems have involved [Cu(X)(L)] complexes where L = pyridine, polypyridines, PPh$_3$, and chelating phosphine ligands and X = Cl, Br, I affording cubane-like Cu$_4$X$_4$L$_4$ clusters and coordination polymers exhibiting luminescent properties.[6−8] Cu(I) complexes with heterocyclic phosphorus donor ligands have shown interesting phosphorescent properties.[8f] Related studies have demonstrated the intriguing luminescent properties of some CuX-based (X = Br, I) coordination polymers containing clusters involving bridging 1,3-dithioether ligands.[9−12]

A great deal of interest has been evoked in the general field of metal 1,1-dithiolates particularly including dithiocarbamates because of their rich structural varieties, interesting conducting, magnetic, and optical properties, uses as metal organic chemical

Received: November 7, 2014
Published: February 20, 2015

DOI: 10.1021/ic502688h

vapor deposition precursors for the preparation of metal sulfides, and myriad applications in agriculture, medicine, and industry.[13] The soft silver(I) and copper(I) ions have strong affinity for the sulfur-based ligands. Many silver(I) mono- and multinuclear thiolato complexes with aesthetic architectures have been explored; however, there are scant reports on Cu(I) complexes with sulfur ligands.[10b,11a−c] The ubiquitous dithiocarbamate ligands can coordinate to a metal via sulfur donor atoms, most commonly in a symmetrical or asymmetrical bidentate, bidentate-bridging and less commonly in a monodentate fashion;[13] the coordination patterns observed in complexes **1**−**3** are given in Figure 1. The multifaceted chemistry and varied properties of the dithiocarbamate complexes may be ascribed to the delocalization that this ligand exhibits in its complexes.[13,14] The coordination chemistry of the neutral dimethyltrithiocarbonate ligand (Figure 2) has been unexplored until now probably because of its poor donor ability.

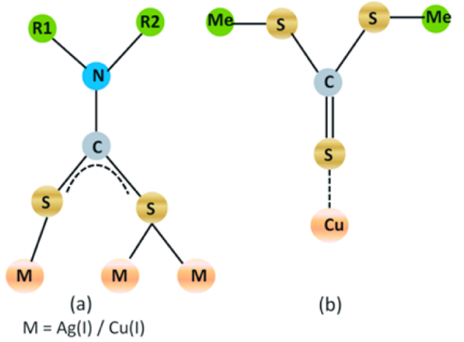


Figure 1. Cartoon representation of coordination patterns. (a) Bidentate-bridging for dithiocarbamate in clusters (**1** and **2**). (b) Monodentate for the neutral dimethyltrithiocarbonate ligand in **3**.

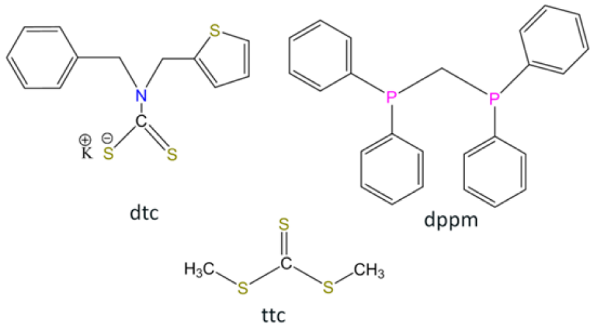


Figure 2. Ligands used in the present work.

Despite their synthetic versatility and practical applications, the coinage metal clusters and coordination polymers (CPs) with dithiocarbamate ligands have not gained as much attention as complexes containing halide ligands in combination with the pyridyl- or even phosphine-based ligands[7,8] likely due to dominant contribution of the resonance form $R_2N^+{=}CS_2^{2-}$, showing S,S-chelating behavior. However, some mixed-valent Cu(I)/Cu(II) dithiocarbamate CPs and their promising semiconductor behavior have been reported.[11a,b] It is therefore critical to make changes to coordination environments about the metal centers utilizing the monoanionic *N*-methylbenzyl-*N*-methylthiophenedithiocarbamate (dtc) and neutral dimethyltrithiocarbonate (ttc) and 1,1-bis(diphenylphosphino)methane (dppm) ligands to map out both the structural and luminescent properties of the fascinating molecules thus obtained. The synthesis, structural investigation, and luminescent and conducting properties of two new clusters and a CP derived from the dtc, iodide, and neutral ttc and dppm ligands (Figure 2) were undertaken, and the results are described in this contribution.

In spite of some obvious similarities, the monoanionic dithiocarbamate and neutral trithiocarbonate ligands differ in several ways: (i) the delocalization that the dithiocarbamate ligands can provide in the complexes resulting in diverse structures and properties is not exhibited by the trithiocarbonate ligand, (ii) weak coordination capability of the −SMe fragment on the trithiocarbonate ligand may facilitate bonding only through the C=S moiety in a monodentate manner, whereas the dtc ligand with negative charge on the S atoms in the dominant resonance structure $R_2N^+{=}CS_2^{2-}$ is commonly S,S-chelating, and (iii) the dithiocarbamate can stabilize the common as well as higher oxidation states, whereas the ttc ligand is expected to form complexes with low-valent soft metal ions. Furthermore, the incorporation of the chelating/bridging dppm ligand may provide a rigid coordination environment about the metal center that may suppress the solvent-mediated rapid dissociation of the emissive excited state and quenching process, an important prerequisite for the prominent photophysical properties of the complexes.

■ EXPERIMENTAL SECTION

Materials and General Methods. All reactions were performed in the open at ambient temperature. The solvents were purified by standard procedures. The reagent grade chemicals used in the experimental work were obtained from commercial sources and used without further purification. The secondary amine required for the synthesis of the dithiocarbamate ligand was prepared by the condensation of benzylamine and thiophene-2-carboxaldehyde to give the corresponding imine, followed by the subsequent reduction with $NaBH_4$. The potassium salts of the dtc and neutral ttc ligands were synthesized by previously reported procedures.[14,15] The experimental details pertaining to the elemental (C, H, N) analysis and IR (KBr), ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and UV−vis spectra are the same as described earlier.[14] Sulfur was determined gravimetrically as $BaSO_4$. Chemical shifts are quoted in parts per million with tetramethylsilane as an internal standard for ^{1}H and ^{13}C NMR and with PCl_3 as an external standard (δ = 220 ppm) for ^{31}P NMR spectra. Time-resolved fluorescence studies were performed[16] on a Ti-Sapphire picosecond laser coupled to a time-correlated single-photon counting setup. The excitation wavelength is 390 nm, which is a frequency-doubled output of the laser at 780 nm. The repetition rate of the laser was 4 MHz. Emission was collected at the quoted wavelengths with emission polarizer at magic angle (54.7°). The instrument response function (IRF) had fwhm of 90 ps. The peak counts for measurement were kept at ∼10 000. The steady-state and solid-state luminescence measurements were done using a fluorolog fluorimeter. Thermogravimetric analysis (TGA) was recorded on a PerkinElmer STV 6000 TG/DTA.

Synthesis and Characterization of Complexes. *[$Ag_6(dtc)_6$] 1.* To a stirred 10 mL methanolic solution of the ligand Kdtc (0.317 g, 1 mmol) was added a 5 mL acetonitrile solution of $AgNO_3$ (0.170 g, 1 mmol), and stirring continued for 3 h. The solid compound thus obtained was removed by filtration, washed with a methanol/ether mixture, and dissolved in dichloromethane to yield block-shaped yellow crystals of **1** within two weeks.

Yield: (0.984 g, 82%). Anal. Calcd for $C_{79}H_{74}Ag_6Cl_2N_6S_{18}$ (2393.46): C 39.49, H 3.10, N 3.50, S 24.02%. Found: C 39.15, H 3.18, N 3.25, S 23.65. IR (KBr, cm^{-1}): 1450 (ν_{C-N}), 1079, 944 (ν_{C-S}). ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 4.35 (s, 2H, $-CH_2-C_4H_3S$), 5.36 (s, 2H, $-CH_2-C_6H_5$), 6.88–7.39 (m, 8H, Ar–H). $^{13}C\{^1H\}$NMR (75.45 MHz, $CDCl_3$, ppm) δ 52.98 ($-CH_2-C_4H_3S$), 58.06 ($-CH_2-C_6H_5$), 126.03–137.32 (Ar–C), 207.50 (CS_2). UV–vis. (CH_2Cl_2, λ_{max} (nm), ε (M^{-1} cm^{-1})): 245.50 (7.62×10^4), 285 (6.73×10^4), 343.60 (1.5×10^4), 400 (4.30×10^3).

$[Cu_3I_2(dppm)_3(dtc)]$ **2.** To a stirred 5 mL dichloromethane solution of dppm (0.198 g, 0.5 mmol) was added a suspension of CuI (0.90 g, 0.5 mmol) in 15 mL of ethanol followed by addition of a 10 mL methanolic solution of Kdtc (0.158 g, 0.5 mmol). The reaction mixture was stirred for ~12 h, giving an off-white precipitate, which was filtered off and dissolved in dichloromethane to give pale yellow crystals of **2** within three weeks.

Yield: (0.675 g, 72%). Anal. Calcd for $C_{88}H_{78}Cu_3I_2NP_6S_3$ (1875.93): C 56.06, H 4.22, N 0.75, S 5.15%. Found: C 55.78, H 4.29, N 0.68, S 4.72. IR (KBr, cm^{-1}): 1482 (ν_{C-N}), 1027, 988 (ν_{C-S}). ^1H NMR (300.40 MHz, $CDCl_3$, ppm): δ 3.36 (s, 6H, $-CH_2-$dppm), 5.28 (s, 2H, $-CH_2-C_4H_3S$), 5.50 (s, 2H, $-CH_2-C_6H_5$), 6.92–7.77 (m, 68H, Ar–H). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm) δ 28.55 ($-CH_2-$, dppm), 50.19 ($-CH_2-C_4H_3S$), 55.25 ($-CH_2-C_6H_5$), 125.63–138.08 (Ar–C), 207.08 (CS_2). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ = −21.66 ppm. UV–vis (CH_2Cl_2, λ_{max} (nm), ε (M^{-1} cm^{-1})): 250 (3.27×10^4), 310 (3.22×10^3), 340 (1.00×10^3).

$[Cu(ttc)I]_\infty$ **3.** A 5 mL solution of the ligand ttc (1.0 mL; in excess) in dichloromethane was added to a suspension of CuI (0.190 g, 1 mmol) in 15 mL of ethanol and stirred for 6 h. The bright orange solid thus formed was filtered off, washed with ethanol, dried in air, and dissolved in acetonitrile to yield needle-shaped orange crystals of **3** within 15 days.

Yield: (0.262 g, 80%). Anal. Calcd for $C_3H_6CuIS_3$ (328.70): C 10.96, H 1.84, S 29.26%. Found: C 10.68, H 1.82, S 28.82%. IR (KBr, cm^{-1}): 1070 ($\nu_{C=S}$), 948, 903 (ν_{C-S}). ^1H NMR (300.40 MHz, CD_3CN, ppm): δ 2.53 (s, 6H, $-SCH_3$). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_3CN, ppm) δ 21.81($-S-CH_3$), 227.20 ($-C{=}S$). UV–vis (CH_3CN, λ_{max} (nm), ε (M^{-1} cm^{-1})): 220 (1.83×10^5), 250 (1.00×10^4), 310 (8.6×10^3), 420 (1.5×10^2).

X-ray Structure Determinations. Single crystals of the complexes **1**–**3** were grown by slow evaporation of the solution of complexes in CH_2Cl_2 (**1** and **2**) and in CH_3CN (**3**). The X-ray diffraction data were collected on an Oxford X-calibur CCD diffractometer at 293 K using Mo Kα radiation. Data reduction was carried out using the CrysAlis program.[17] The structures were solved by direct methods using SHELXS-97[18] and refined on F^2 by full-matrix least-squares method using SHELXL-97.[19] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically fixed with displacement parameters equivalent to 1.2 times that of the atoms to which they were bonded. In **1**, the position of the sulfur atom in a thiophene ring was disordered over two positions. A solvent dichloromethane molecule was given 50% occupancy. In **2**, one of the iodides in a general position was refined with 50% occupancy, while one ligand was disordered with the thiophene and phenyl rings disordered over two positions. Diagrams for all complexes were prepared using ORTEP[20] and Mercury software.

■ RESULTS AND DISCUSSION

General and Spectroscopy. Complexes **1**–**3** were obtained in good yield by the treatment of a solution of the ligands Kdtc/dppm/ttc and metal salts $AgNO_3$/CuI in equimolar ratios. Note that the reaction of $AgNO_3$ with dppm and Kdtc, $AgNO_3$ with ttc, and CuI with Kdtc did not yield the single crystals of the desired new products. The complexes are air- and moisture-stable. The complexes were characterized by IR, UV–vis, ^1H, ^{13}C, and ^{31}P NMR spectroscopies. The attractive structural features of the Ag(I) **1** and Cu(I) **2** clusters and the CP **3** were investigated by X-ray crystallography. Complex **1** has a spectacularly arranged Ag_6S_6 core. Complex **2** exhibits varied environments about the three Cu(I) centers provided by the dtc, dppm, and I^- ligands. Complex **3** is a Cu–I-based one-dimensional (1-D) CP having a "staircase"-like structure with the ttc ligands occupying peripheral positions on the metal centers. Their luminescence behavior in solution and in the solid state, including luminescence lifetimes, was studied. The short mean lifetimes are indicative of rapid decay of the photoexcited states. The semiconducting behavior of the complexes was estimated by the diffuse reflectance spectra, and their thermal behavior was studied through thermogravimetric differential thermal analysis (TG-DTA).

In the IR spectra, complexes **1** and **2** show $\nu_{(C-N)}$ and $\nu_{(C-S)}$ vibrations at 1450, 1482 cm^{-1} and at 944–1079 cm^{-1}, whereas **3** shows the $\nu_{(C-S)}$ vibrations at 1042, 948, and 903 cm^{-1} diagnostic of dithiocarbamate and ttc ligands. The ^1H NMR spectra of all the complexes show resonances characteristic of the ligand functionalities, which integrate well to the corresponding protons. In the ^{13}C NMR spectra of **1** and **2** the NCS_2 carbon is observed at δ (207.50, 207.80) ppm, while in **3** the CS_3 carbon occurs at δ 227.80 ppm. A single resonance observed at δ −21.66 ppm in the ^{31}P NMR spectra of **2** for all the phosphorus atoms of the ligand dppm is indicative of P,P coordination.

*Crystal Structure of **1**, $[Ag_6(dtc)_6]$.* Crystallographic data, structure refinement details, and selected bond distances and angles of **1**–**3** are presented in Tables S1–S4 (Supporting Information). The hexameric complex **1** contains a crystallographic center of symmetry; each asymmetric unit is composed of half of a discrete molecule containing three Ag and six S atoms from three dithiocarbamate ligands along with a solvent dichloromethane molecule with 50% occupancy (Figure 3a). In the asymmetric unit three dithiocarbamate ligands are uniquely bonded to three silver atoms in a bidentate-bridging fashion constructing a crownlike shape, virtually similar to S_6 (Figure 3b). We first consider the unique Ag_3S_6 core in the asymmetric unit. The three Ag⋯Ag distances are Ag(1)–Ag(2) 2.966(1),

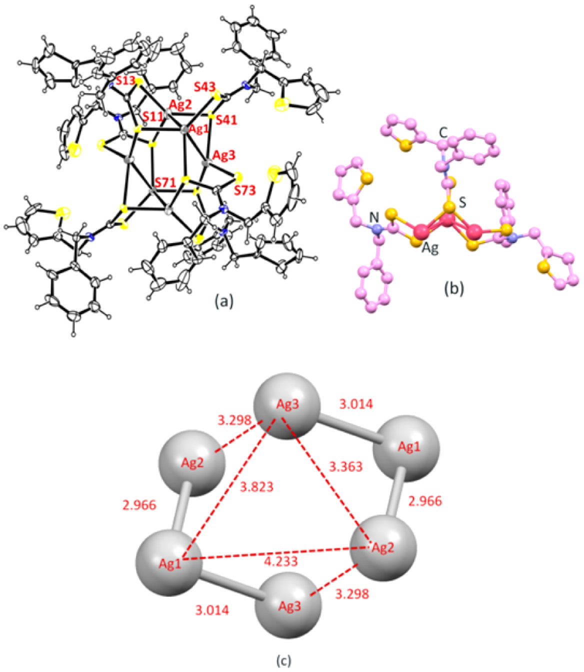


Figure 3. (a) The centrosymmetric structure of **1** with ellipsoids shown at 20% probability. The solvent dichloromethane is not shown. (b) Asymmetric unit showing the central Ag_3S_6 crownlike core. (c) Ag–Ag contacts (distances in Å) in hexanuclear core of **1**.

Ag(1)−Ag(3) 3.014(1), and Ag(2)−Ag(3) 3.363(1) Å, all of which are smaller than the sum of van der Waals radius[21] for the silver atoms (3.44 Å), thereby indicating weak argentophilic interactions, at least in the first two shorter interactions (Figure 3c). This structure can be directly compared to two other silver hexamers whose crystal structures have been determined, namely, the complex anion[12] $[Ag(mna)]_6^{6-}$ (mna = mercaptonicotinate)], **1**′; and $Ag_6(Pr_2dtc)_6$, **1**″.[11d,e] Both **1**′ and **1**″, like **1**, are centrosymmetric. The cores of **1** and **1**′ are compared in Figure 4a,b, respectively.

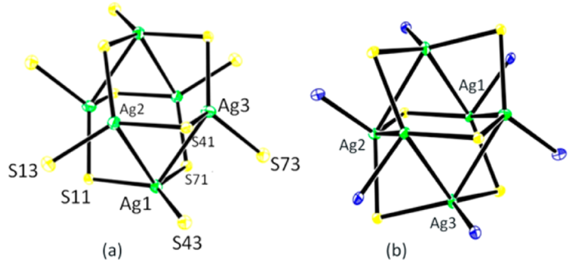


Figure 4. A comparison of the structural cores of (a) **1** and (b) **1**′. The numbering system of **1**′ in (b) is taken from the literature. Using the nomenclature from (a), comparable distances (Å) in **1**, **1**′ and **1**″ (not shown) are Ag1−Ag2, 2.966(1), 2.988(1), 2.905(5); Ag1−Ag3 3.014(1), 3.032(1), 2.965(5); Ag2−Ag3, 3.363(1), 3.382(1), 3.199(5); Ag1−Ag2′ 4.233(1), 3.356(1), 4.014(5); Ag1−Ag3′ 3.823(1), 3.348(1), 3.849(5) ; Ag2−Ag3′ 3.298(1), 2.937(1), 3.446(5). Remaining distances are >4.2 Å.

It will be apparent from Figure 4 that the coordination pattern of the ligands is equivalent in **1** and **1**′. However, there are significant differences in the distances between silver atoms. In particular, there are three independent short distances <3.05 Å in **1**′, while only two such distances are in **1**. In general, apart from the two shortest interactions, all the Ag···Ag distances are longer in **1** than in **1**′. It seems likely this difference is due to the disparity in ligand bites as the mean S···S distance in **1** is 3.03 Å, while the S···N distance in **1**′ is far less at 2.69 Å.

The structure of **1**″ has been reported twice, an early report[11e] and a later more detailed study.[11d] Analysis of the coordinates of the early report show it to be approximately equivalent to both **1** and **1**′, though closer to the former as shown in the dimensions listed in the caption to Figure 4. In **1** all three unique silver atoms are bonded to three sulfur atoms with similar distances ranging from 2.435(3) to 2.553(2) Å. The metal atoms Ag(1), Ag(2), and Ag(3) are 0.211(2), 0.257(2), and 0.530(2) Å, respectively, from the plane of the three sulfur atoms; thus, they can be considered as having distorted trigonal geometry. The two asymmetric units containing a Ag_3S_6 core are connected through the Ag−S bonds Ag2−S71′ (′ = 1 − x, 1 − y, 1 − z) and Ag3−S11′ at 2.548(3) and 2.506(2) Å, respectively. The Ag−S distances in the range of 2.435(3)−2.550(3) Å are well within the range for the analogous silver thiolato complexes.[11d−f,12] The complete Ag_6S_6 core presents a distorted hexagonal ring-shaped structure with alternating silver and sulfur atoms. In the hexameric core each Ag_3S_3 unit almost perfectly overlaps the other in a highly symmetric manner (Figure 5). The S···H (2.99 Å), Cl···π (4.27 Å), and C−H···π (2.71 Å) weaker interactions stabilize the supramolecular framework of the cluster.

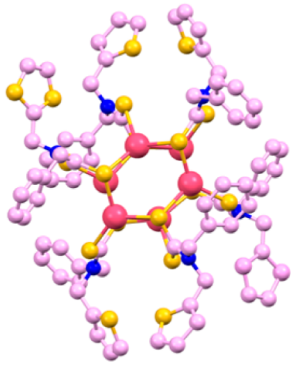


Figure 5. Molecular structure of **1** showing the hexagonal Ag_6S_6 core with alternating Ag and S atoms. The dichloromethane molecule has been omitted for clarity.

Crystal Structure of **2**, *[$Cu_3I_2(dppm)_3(dtc)$].* **2** is a unique trinuclear heteroleptic cluster complex formed with distinctly soft Cu(I) and dithiocarbamate, dppm and iodide ligands (Figure 6a). The asymmetric unit contains a complete molecule with two iodide ions outside the coordination sphere. There are three independent iodides in the asymmetric unit, I1 and I2 in general positions and I3 on a 2-fold axis. However, I2 was successfully refined with 50% occupancy and therefore the three independent copper atoms were confirmed as being Cu(I), a fact consistent with bond lengths.

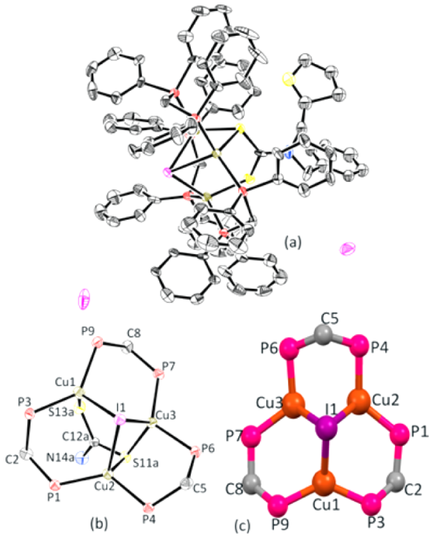


Figure 6. ORTEP representation of **2** with displacement ellipsoids at 30% probability. (b) Clear view of the $Cu_3I_1P_3S_2$ core. (c) The three hexagonal fused rings at the core of the trinuclear molecule.

The geometry around each metal center is distorted tetrahedral as is evident from the angles in the range of 95.55(11)−133.71(12)° (Supporting Information, Table S3); maximum distortion from the tetrahedral geometry is observed at the Cu1 center with the P3−Cu1−P9, P3−Cu1−S13A, S13A−Cu1−P9, P9−Cu1−I1, P3−Cu1−I1, and S13A−Cu1−I1 angles at 133.71(12), 95.55(11), 96.19(11), 104.69(9), 104.35(9), and 125.29(9)°, respectively. The overall coordination environment about each metal center is defined by two P atoms, one each from two adjacent dppm molecules, one iodine atom, which is common to all three metal centers, and one sulfur atom from a dtc ligand. Atom S11A of the dtc ligand is bonded to Cu2 and Cu3, while S13A is solely linked to the Cu1 center; thus, the dtc ligand is coordinated in a bidentate-bridging fashion linking the three metal centers. The Cu2−

S11A and Cu3−S11A bonds are shorter and nearly equal at 2.357(3) and 2.323(3) Å, respectively, whereas the Cu1−S13A distance is slightly longer at 2.385(3) Å though all are within the literature range.[9,10,11a−c] Each dppm ligand is bonded to two metal centers unsymmetrically in a μ^2-bridging fashion with Cu−P distances in the 2.252(3)−2.280(3) Å range[7,8] (Table S3). The Cu−I distances[6] are in the order Cu2−I1 > Cu1−I1 > Cu3−I1 at 2.769(14) > 2.723(1) > 2.707(14) Å. The Cu2−Cu3 distance at 2.906(2) Å is significantly shorter than the Cu1−Cu2 and Cu3−Cu1 distances at 3.551(2) and 3.338(2) Å, respectively, which are longer than the sum of the van der Waals radii (2.8 Å), showing the presence of somewhat weak Cu···Cu bonding.[8,11a−c,21] The core is comprised of three fused distorted hexagonal rings with the I1 atom located at the center of three rings and is above the Cu_3 plane by 1.963(1) Å, Figure 6c. The iodine atom caps the triangle from one side forming a Cu_3I_1 tetrahedron and the two sulfur atoms of the dtc ligand cap from the other side (Figure 6b).

In **2**, the C12A−N14A distance at 1.379(14) Å is slightly longer than that observed in **1** (1.338(10) Å) though both are intermediate within C−N single and double bond showing dominant contribution of the resonance form $R_2N^+{=}CS_2^{2-}$ of the dtc ligand. In **1** and **2** the C−S distances in the range of 1.695(9)−1.754(9) Å are somewhat shorter than the C−S single bond (ca. 1.81 Å) due to delocalization over the NCS_2 moiety.

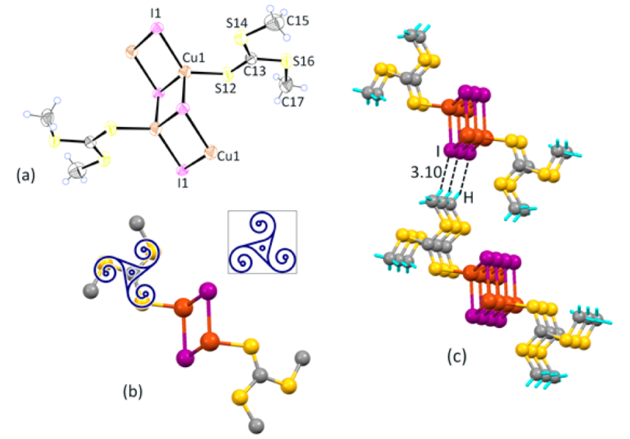


Figure 7. (a) ORTEP representation of **3** with displacement ellipsoids at 50% probability. (b) The twisted peripheral ttc appendages resembling triskelion shape (shown in inset). (c) Interlinking of polymeric chains via C−H···I interactions (3.10 Å) in the supramolecular structure.

*Crystal Structure of **3**, [Cu(ttc)I]$_\infty$.* The crystal structure of **3** is based upon the Cu−I scaffold (Figure 7a). The asymmetric unit is comprised of a single Cu(I), I$^-$, and a trithiocarbonate (ttc) ligand in 1:1:1 ratio generating a 1-D coordination polymer. The metal is uniquely bonded to three iodine atoms and a S atom from the C=S fragment of the ttc ligand peripherally establishing a distorted tetrahedral geometry about the metal. The three I−Cu−I angles are at 105.36(3)°, 107.90(4)°, and 109.56(3)°; three S−Cu−I angles are at 99.12(6)°, 106.62(6)°, and 127.50(6)°. The central Cu(I) ion is 0.968 Å above the mean I−I−I plane toward the −C=S sulfur atom of the ttc ligand. The overall structure is a staircaselike ABABAB arrangement (Figure 7a) with A and B representing two fused Cu_2I_2 centrosymmetric parallelograms that intersect at 105.36(3)°. The two parallelograms show slightly different dimensions; in one, the unique Cu−I bond length is 2.612(1) Å, and in the other it is 2.667(1) Å, while the shared Cu−I bond length is 2.732(1) Å. The unique internal angles in the two parallelograms are 107.90(4) and 109.56(3)°, respectively. The S atoms of the C=S fragments of the neutral ttc ligands are rather weakly bonded with the Cu1−S12 distance of 2.268(2) Å.[9,11a−c] The −SMe appendages at ttc ligands are oriented to form a "triskelion"-like shape (Figure 7b) in this structure. The Cu···Cu distances at 3.114(1) and 3.146(1) Å are somewhat longer than expected for any significant cuprophilic interaction.[8,11a−c,21] The S···S separations of 4.035 and 4.052 Å show weak intra- and intermolecular S···S contacts, respectively. The supramolecular structure of the polymer is sustained by significant C−H···I (3.105 Å) hydrogen bonding interactions linking together the two polymeric chains (Figure 7c). Note that the less common three-coordinate iodine atom is observed in both **2** and **3**.

Absorption and Emission Spectra. The electronic absorption spectra of **1** and **2** in dichloromethane and **3** in acetonitrile solution are displayed in Figure 8. The solid-phase absorption spectra were recorded as Nujol mull (Figure S5, Supporting Information). The complexes exhibit medium to strong absorptions near 350 (1.50 × 10^4 (**1**), 1.00 × 10^3 (**2**) M^{-1}cm^{-1}), 300 (6.73 × 10^4 to 8.6 × 10^3 M^{-1} cm^{-1} (**1**−**3**)), 250 (7.62 × 10^4 to 1.00 × 10^4 M^{-1} cm^{-1} (**1**−**3**)), and 215 (1.83 × 10^5 M^{-1} cm^{-1} (**3**)) nm. The Ag_6 cluster **1** and the Cu(I) coordination polymer **3** exhibit a red-shifted band near 400 nm (4.30 × 10^3 (**1**), 1.5 × 10^2 (**3**) M^{-1} cm^{-1}). The feature of the spectra in solution almost matches solid-state spectra indicating similar structures persist in solution. The high-energy bands below 300 nm are assigned to ligand-centered $\pi-\pi^*$ transitions, whereas those in the 300−400 nm region are assigned to metal-to-ligand, Cu-phosphine/dithio ligand (MLCT) with some admixture of halogen (I$^-$)-to-ligand (XLCT) states.[8d,e,11d,22]

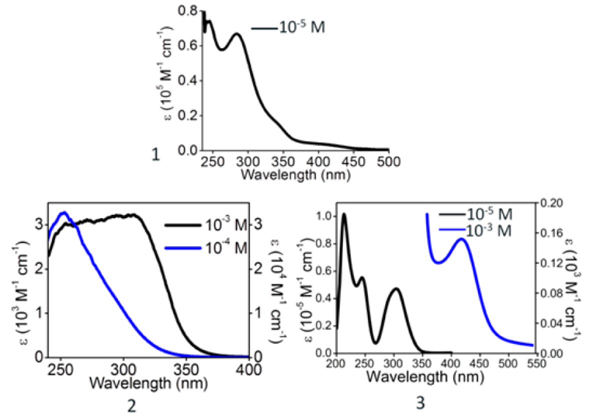


Figure 8. Absorption spectra of complexes **1**−**3** in solution.

When excited at λ_{exc} 395 nm in dichloromethane solution at room temperature the Ag_6 cluster **1** shows a strong unstructured emission band at λ_{em}^{max} = 500 nm (Figure 9a), whereas at λ_{ex} 330 nm in the solid state it displays a strong blunt emission band with emission maxima at λ_{em}^{max} 500 nm (Figure 9b) arising from the metal-perturbed intraligand states. This difference in features of emission band may be attributed to some intramolecular forces in the two phases. The significant Stokes shift of 170 nm may be attributed to the closer Ag···Ag interactions in the highly rigid and robust cluster structure of **1** in the solid state.[2c−e] Note that **1** luminesces both in solution

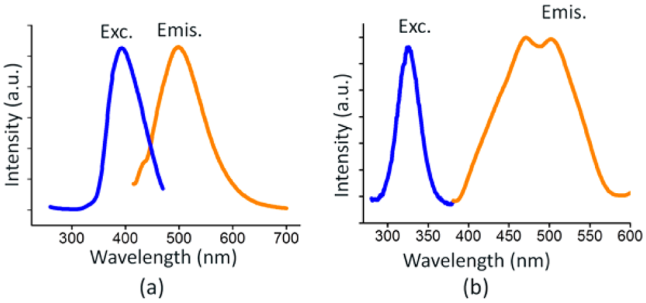


Figure 9. (a) Excitation and emission spectra of **1** in solution at room temperature, λ_{exc} = 395 nm; λ_{em}^{max} = 500 nm. (b) Emission spectra of **1** in solid state λ_{exc} = 330 nm and λ_{em}^{max} = 500 nm.

and solid phases at room temperature, while the previously reported hexameric $Ag_6(^nPr_2dtc)_6$ cluster complex[11d] exhibits luminescence in toluene solution, only at 77 K.

Upon excitation at 390 nm in solution, **2** shows an emission maxima at 450 nm with vibronic feature[9] (Figure 10a), while at λ_{exc} = 330 nm in solid an unstructured emission band at λ_{em}^{max} = 460 nm is observed (Figure 10b) with a significant Stokes shift of 130 nm arising from the dCu–π^* (dppm) with some admixture of iodide-dppm/dtc CT state.[7,8] The vibronic feature of this compound is resolved in solution due to some structural reorganization that does not happen in the solid state between the ground and excited states.[7a,b]

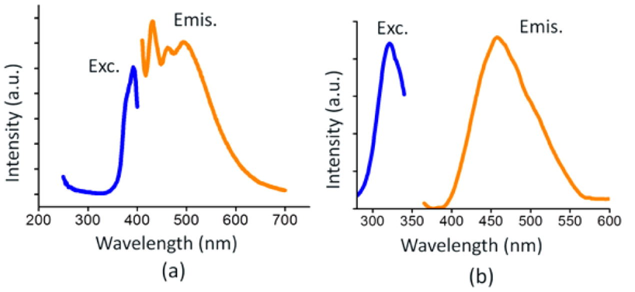


Figure 10. (a) Excitation and emission spectra of **2** in solution at room temperature, λ_{exc} = 390 nm; λ_{em}^{max} = 450 nm and another weak emission at 500 nm. (b) Emission spectra of **2** in solid state λ_{exc} = 330 nm and λ_{em}^{max} = 460 nm.

It is worth noting that bright orange CP **3** based upon Cu(I)-iodide scaffold does not luminesce both in solid and solution. Unlike previously reported luminescent Cu_4X_4 (X = Cl, Br, I) CPs containing N-[7e] and even S-donor ligands[9,10] the nonluminescent characteristics of **3** may be attributed to the dimethyltrithiocarbonate moiety bonded to Cu(I) at peripheral positions presumably acting as a quencher.

The time-resolved emission measurement, performed at room temperature in solution (λ_{exc} = 390 nm), revealed triexponential curve (Figure 11) for both **1** and **2** having lifetimes τ_1–τ_3 with amplitudes α_1–α_3 as summarized in Table 1. This behavior may be attributed to crystallographic independence of some fragment(s) and heterogeneity in the ligand environments.[7a–d] The mean lifetime of the clusters is short (0.331 and 0.490 ns) indicating their fluorescence behavior.[7] Somewhat longer lifetime of **2** in comparison to **1** may be attributed to more rigid coordination environment in the former due to the presence of bulky bridging dppm ligands.[7a] In a recent report some sulfur-containing Ag(I)/Cu(I) complexes have been found to possess significantly long-lived excited state having much longer lifetime compared to **1** and **2**. This feature of the reported complexes is attributable to quite short Ag–Ag and Cu–Cu distances.[7f]

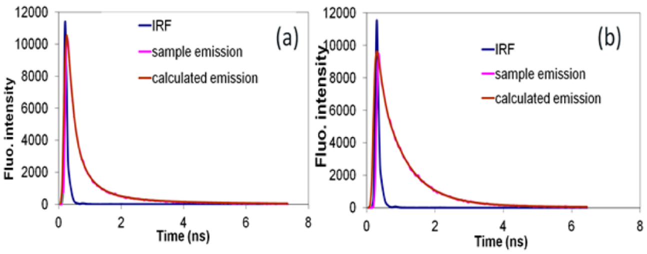


Figure 11. Time-resolved decay profiles for (a) Ag_6 cluster **1** and (b) Cu(I) cluster **2**.

Table 1. Results for Lifetime Measurements at Room Temperature

compound	τ_1 (α_1)[a]	τ_2 (α_2)[a]	τ_3 (α_3)[a]	τ_m[b]
1	2.459(0.035)	0.519(0.273)	0.148(0.692)	0.331
2	2.713(0.022)	0.096(0.469)	0.757(0.509)	0.490

[a] α_i is the amplitude for the fluorescence lifetime τ_i. [b] The mean lifetime (τ_m) is calculated by the equation $\tau_m = \sum \alpha_i \tau_i$. τ is reported in ns.

Diffuse Reflectance Spectra. The diffuse reflectance spectra were obtained using $BaSO_4$ as standard at ambient temperature to evaluate the band gap of the complexes (Figure 12). The band gap (E_g) for **1**–**3** was found to be 2.12, 3.01 and 2.18 eV, respectively, and calculated using the Planck relationship, that is, $E_g = h\nu = hc/\lambda$, where h is Planck's constant (4.1357×10^{-15} eV s), c is the velocity of light (2.998×10^8 m/s), and λ is the wavelength (nm). The suitable wavelength for band-gap determination was ascertained by the first differential of diffuse reflectance spectra and was found to be 583, 412, and 568 nm for **1**–**3**, respectively, as shown in the inset of Figure 12. The calculated band gap values are consistent with the semiconducting nature of the complexes.[23]

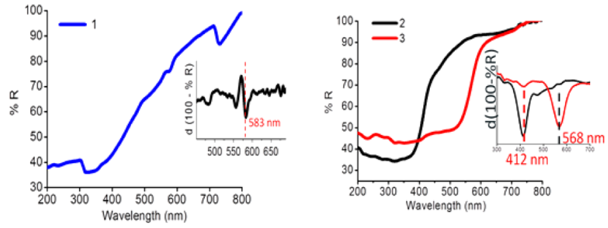


Figure 12. Diffuse reflectance spectra of **1**–**3**. (inset) The first differential.

Thermal Studies. The TGA curves (Figure 13, Table 2) of **1** and **2** show one-step decomposition in the 160–420 °C and 227–450 °C temperature range with weight loss of 91.5% and 80% leaving the residue of AgS and CuI_2 respectively. Complex **3** shows a two-step decomposition process. First from 82 to 162 °C with 60% weight left corresponding to CuI (calcd. 58%) and is stable until 540 °C. In the final step beyond 540 °C there is a sharp loss in weight until 700 °C with the formation of volatiles where no residual is observed at temperature above 700 °C. It is noteworthy that only in **2** the metal Cu(I) is oxidized into Cu(II) in the residue formed.

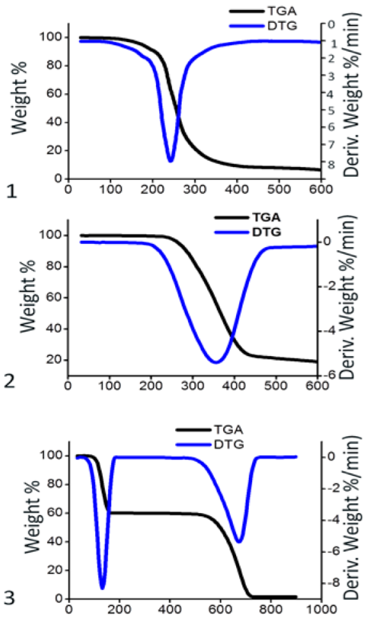


Figure 13. TG-DTA curves for complexes **1**−**3**.

Table 2. TGA Results for the Complexes

compound	*T*, °C in TGA	residue wt. observed (calcd.) (%)	expected product of decomposition
1	160−420	8.5 (5.82)	AgS
2	227−450	20 (17)	CuI_2
3	82−160	60 (58)	CuI

■ CONCLUSIONS

The new homoleptic $Ag_6(dtc)_6$ **1** and heteroleptic $[Cu_3I_2(dppm)_3(dtc)]$ **2** clusters and a coordination polymer $[Cu(I)(ttc)]_\infty$ **3** have been fully characterized, and their solid-state structures and luminescent properties have been investigated. X-ray crystallography revealed spectacular structures highlighting the versatility of the metal−ligand systems in these complexes. **1** is hexanuclear with alternating Ag(I) and S atoms, whereas **2** is trinuclear with an array of Cu(I), P, I, and S atoms at the core. The dtc ligand coordinates as a bidentate-bridging ligand in both **1** and **2**. The ttc ligand in **3** is linked at a peripheral position to the metal center forming a CP with a staircaselike structure. In **1** and **2** the intermetallic distances are slightly too long to represent any significant intermetallic bonding and are even longer in **3**. Clusters **1** and **2** show impressive fluorescent behavior in solid and solution due to conformational rigidity and metal−metal interactions, while **3**, despite being a Cu(I)-iodide based polymer, is nonluminescent in either of the two phases contrary to the reported Cu(I)−iodide-based heteroleptic polymers. This may be attributed to the ttc ligands acting as a quencher at Cu(I) centers. The fluorescent lifetime of **2** is somewhat higher than **1** owing to greater steric bulk and rigidity of ligands in the former; these factors are critical in the design of luminescent materials with significant lifetime of the emissive excited states. The band-gap values are indicative of semiconducting behavior of the complexes **1**−**3**. This study expands the scope of sulfur/halide/phosphine ligand-based clusters and CPs with group 11 metal ions for their intriguing structures and applications as functional materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files (CIFs). Tabulated crystal parameters and refinement data, tabulated selected bond lengths and angles for **1**−**3**, illustration of electronic absorption spectra in solid phase. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nsinghbhu@gmail.com or nsingh@bhu.ac.in. Fax: +91-542-2386127.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial supports from the Council of Scientific and Industrial Research (CSIR), New Delhi, Project No. 01 (2679)/12/EMR-II (NS, MKY) and SRF (GR) are gratefully acknowledged, and the Department of Chemistry, CAS-UGC-I, Banaras Hindu University, is gratefully acknowledged for the use of X-ray facilities. Prof. G. Krishnamoorthy and Ms. M. Kombhabhail are gratefully acknowledged for time-resolved luminescence study at TIFR, Mumbai, India.

■ REFERENCES

(1) (a) Safin, D. A.; Mdluti, P. S.; Revaprasadu, N.; Ahmad, K.; Afzal, M.; Helliwell, M.; O'Brien, P.; Shakirova, E. R.; Babashkina, M. G.; Klein, A. *Chem. Mater.* **2009**, *21*, 4233. (b) Kutal, C. *Coord. Chem. Rev.* **1990**, *99*, 213. (c) Yam, V. W. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999**, *28*, 323. (d) Yam, V. W.-W.; Lo, K. K.-W.; Wang, C.-R.; Cheung, K.-K. *Inorg. Chem.* **1996**, *35*, 5116. (e) Catalano, V. J.; Kar, H. M.; Garmas, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1979. (f) Su, W. P.; Hong, M. C.; Weng, J. B.; Cao, R.; Lu, S. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2911. (g) Quaroni, L.; Chumanov, G. *J. Am. Chem. Soc.* **1999**, *121*, 10642. (h) Fernandez, E. J.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Rodriguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Chem.—Eur. J.* **2000**, *6*, 636. (i) Naeem, S.; Serapian, S. A.; Toscani, A.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2014**, *53*, 2404.

(2) (a) Yam, V. W.-W; Fung, W. K.-M.; Cheung, K.-K. *Chem. Commun.* **1997**, *1*, 963. (b) Che, C.-M.; Mao, Z.; Miskowski, V. M.; Tse, M.-C.; Chan, C.-K.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4084. (c) Che, C.-M.; Tse, M.-C.; Chan, M. C. W.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. *J. Am. Chem. Soc.* **2000**, *122*, 2464. (d) Barbieri, A.; Accorsi, G.; Armaroli, N. *Chem. Commun.* **2008**, *19*, 2185. (e) Yam, V. W.-W.; Wong, K. M.-C. *Chem. Commun.* **2011**, *47*, 11579. (f) Castineiras, A.; Pedrido, R. *Inorg. Chem.* **2009**, *48*, 4847. (g) Sun, D.; Liu, F.-J.; Huang, R.-B.; Zheng, L.-S. *Inorg. Chem.* **2011**, *50*, 12393. (h) Houser, R. P.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 2101. (i) Browm, E. C.; B-Nahum, I.; York, J. T.; Aboelella, N. W.; Tolman, W. B. *Inorg. Chem.* **2007**, *46*, 486.

(3) (a) Yang, J.-H.; Zheng, S.-L.; Yu, X.-L.; Chen, X.-M. *Cryst. Growth Des.* **2004**, *4*, 831. (b) Pyykko, P. *Chem. Rev.* **1997**, *97*, 597. (c) Tong, M.-L.; Chen, X.-M.; Ye, B.-H.; Ji, L.-N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2237. (d) Tong, M.-L.; Chen, X.-M. *Inorg. Chem. Commun.* **2000**, *3*, 694. (e) Tong, M.-L.; Shi, J.-X.; Chen, X.-M. *New J. Chem.* **2002**, *26*, 814. (f) Sun, D.-F.; Cao, R.; Weng, J.-B.; Hong, M.-C.; Liang, Y.-C. *J. Chem. Soc., Dalton Trans.* **2002**, *3*, 291. (g) Fan, J.; Sun, W.-Y.; Okamura, T.; Xie, J.; Tang, W.-X.; Ueyama, N. *New J. Chem.* **2002**, *26*, 199. (h) Awaleh, M. O.; Baril-Robert, F.; Reber, C.; Badia, A.; Brisse, F. *Inorg. Chem.* **2008**, *47*, 2964.

(4) (a) Young, A. G.; Hanton, L. R. *Coord. Chem. Rev.* **2008**, *252*, 1346. (b) Antonioli, B.; Bray, D. J.; Clegg, J. K.; Gloe, K.; Kataeva, O.; Lindoy, L. F.; McMurtrie, J. C.; Steel, P. J.; Sumby, C. J.; Wenzel, M.

Dalton Trans. **2006**, *40*, 4783. (c) Dong, Y.-B.; Ma, J.-P.; Huang, R.-Q.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2003**, *42*, 294. (d) Jin, X.; Xie, X.; Qian, H.; Tang, K.; Liu, C.; Wang, X.; Gong, Q. *Chem. Comm* **2002**, *6*, 600. (e) Chen, J.-X.; Xu, Q.-F.; Xu, Y.; Zhang, Y.; Chen, Z.-N.; Lang, J.-P. *Eur. J. Inorg. Chem.* **2004**, *21*, 4247. (f) Fijolek, H. G.; Gonzalez-Duarte, P.; Park, S. H.; Suib, S. L.; Natan, M. J. *Inorg. Chem.* **1997**, *36*, 5299.

(5) (a) Ford, P. C.; Vogler, A. *Acc. Chem. Res.* **1993**, *26*, 220. (b) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625. (c) Kyle, K. R.; Ryu, C. K.; DiBenedetto, J. A.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 2954. (d) Haasnoot, J. G. *Coord. Chem. Rev.* **2000**, *131*, 200. (e) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, *35*, 555.

(6) (a) Subramanian, L.; Hoffmann, R. *Inorg. Chem.* **1992**, *31*, 1021.

(7) (a) Cuttell, D. G.; Kuang, S.-M.; Fanwick, P. E.; McMillin, D. R.; Walton, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 6. (b) Makal, A.; Benedict, J.; Trzop, E.; Sokolow, J.; Fournier, B.; Chen, Y.; Kalinowski, J. A.; Graber, T.; Henning, R.; Coppens, P. *J. Phys. Chem. A* **2012**, *116*, 3359. (c) Zink, D. M.; Baumann, T.; Friedrichs, J.; Nieger, M.; Brase, S. *Inorg. Chem.* **2013**, *52*, 13509. (d) Araki, H.; Tsuge, K.; Sasaki, Y.; Ishizaka, S.; Kitamura, N. *Inorg. Chem.* **2005**, *44*, 9667. (e) Pospisil, J.; Jess, I.; Nather, C.; Necasa, M.; Taborsky, P. *New J. Chem.* **2011**, *35*, 861. (f) Lane, A. C.; Vollmer, M. V.; Laber, C. H.; Melgarejo, C. Y.; Chiarella, G. M.; Fackler, J. P., Jr.; Yang, X.; Baker, G. A.; Walensky, J. R. *Inorg. Chem.* **2014**, *53*, 11357.

(8) (a) Fackler, J. P., Jr.; Lopez, C. A.; Staples, R. J.; Wang, S.; Winpennya, R. E. P.; Lattimer, R. P. *J. Chem. Soc., Chem. Commun.* **1992**, *2*, 146. (b) Liu, C. W.; Pitts, J. T.; Fackler, J. P., Jr. *Polyhedron* **1997**, *16*, 3899. (c) Marsich, N.; Nardin, G.; Randaccio, L. *J. Am. Chem. Soc.* **1973**, *95*, 4053. (d) Czerwieniec, R.; Yu, J.; Yersin, H. *Inorg. Chem.* **2011**, *50*, 8293. (e) Perruchas, S.; Tard, C.; Le Goff, X. F.; Fargues, A.; Garcia, A.; Kahlal, S.; Saillard, J.-Y.; Gacoin, T.; Boilot, J.-P. *Inorg. Chem.* **2011**, *50*, 10682. (f) Roesch, P.; Nitsch, J.; Lutz, M.; Wiecko, J.; Steffan, A.; Muller, C. *Inorg. Chem.* **2014**, *53*, 9855.

(9) Knorr, M.; Guyon, F.; Khatyr, A.; Strohmann, C.; Allain, M.; Aly, S. M.; Lapprand, A.; Fortin, D.; Harvey, P. D. *Inorg. Chem.* **2012**, *51*, 9917.

(10) (a) Fackler, J. P., Jr.; Staples, R. J.; Liu, C. W.; Stubbs, R. T.; Lopez, C.; Pitts, J. T. *Pure Appl. Chem.* **1998**, *70*, 839. (b) Liao, P.-K.; Fang, C.-S.; Edwards, A. J.; Kahlal, S.; Saillard, J.-Y.; Liu, C. W. *Inorg. Chem.* **2012**, *51*, 6577.

(11) (a) Okubo, T.; Tanaka, N.; Kim, K. H.; Yones, H.; Maekawa, M.; K-Sowa, T. *Inorg. Chem.* **2010**, *49*, 3700. (b) Okubo, T.; Tanaka, N.; Kim, K. H.; Anma, H.; Seki, S.; Saeki, A.; Maekawa, M.; K-Sowa, T. *Dalton Trans.* **2011**, *40*, 2218. (c) Hesse, R.; Aava, U. *Acta Chem. Scand.* **1970**, *24*, 1355. (d) Sabin, F.; Ryu, C. K.; Ford, P. C.; Vogler, A. *Inorg. Chem.* **1992**, *31*, 1941. (e) Hesse, R.; Nilson, L. *Acta Chem. Scand.* **1969**, *23*, 825. (f) Jennische, P.; Hesse, R. *Acta Chem. Scand.* **1971**, *25*, 423.

(12) Tsyba, I.; B-kit. Mui, B.; Bau, R.; Noguchi, R.; Nomiya, K. *Inorg. Chem.* **2003**, *42*, 8028.

(13) (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301. (b) Hogarth, G. *Prog. Inorg. Chem.* **2005**, *53*, 71. (c) Tiekink, E. R. T.; Haiduc, I. *Prog. Inorg. Chem.* **2005**, *54*, 127. (d) Heard, P. J. *Prog. Inorg. Chem.* **2005**, *53*, 268. (e) Cookson, J.; Beer, P. D. *Dalton Trans.* **2007**, *15*, 1459. (f) Alam, N.; Hill, M. S.; K-Kohn, G.; Zeller, M.; Mazhar, M.; Molloy, K. C. *Chem. Matter.* **2008**, *20*, 6157. (g) O'Brien, P.; Waters, J. *Chem. Vap. Deposition* **2006**, *12*, 620. (h) Mensforth, E. J.; Hill, M. R.; Batten, S. R. *Inorg. Chim. Acta* **2013**, *403*, 9. (i) Zhao, Y.; Perez-Segarra, W.; Shi, Q.; Wei, A. *J. Am. Chem. Soc.* **2005**, *127*, 7328. (i) Fackler, J. P. *Inorg. Chem.* **2002**, *41*, 6959.

(14) (a) Singh, N.; Kumar, A.; Prasad, R.; Molloy, K. C.; Mahon, M. F. *Dalton Trans.* **2010**, *39*, 2667. (b) Rajput, G.; Singh, V.; Singh, S. K.; Prasad, L. B.; Drew, M. G. B.; Singh, N. *Eur. J. Inorg. Chem.* **2012**, *24*, 3885. (c) Singh, B.; Drew, M. G. B.; K-Kohn, G.; Molloy, K. C.; Singh, N. *Dalton Trans.* **2011**, *40*, 623. (d) Kumar, A.; Chauhan, R.; Molloy, K. C.; K-Kohn, G.; Bahadur, L.; Singh, N. *Chem.—Eur. J.* **2010**, *16*, 4307. (e) Singh, V.; Chauhan, R.; Gupta, A. N.; Kumar, V.; Drew, M. G. B.; Bahadur, L.; Singh, N. *Dalton Trans.* **2014**, *43*, 4752. (f) Rajput, G.; Singh, V.; Gupta, A. N.; Yadav, M. K.; Kumar, V.; Singh, S. K.; Prasad, A.; Drew, M. G. B.; Singh, N. *CrystEngComm* **2013**, *15*, 4676.

(15) Lee, A. W. M.; Chan, W. H.; Wong, H. C. *Synth. Commun.* **1988**, *18*, 1531.

(16) Krishnamoorthy, G. *J. Mol. Biol.* **2009**, *393*, 735.

(17) Oxford Diffraction. *CrysAlis CCD, RED,* version 1.711.13; Oxford Diffraction Poland Sp. (Agilent Technologies): Wroclaw, Poland (Santa Clara, CA), 1995−2003.

(18) Sheldrick, G. M. *SHELXS97,* Program for Crystal Structure Solution; University of Gottingen: Gottingen, Germany, 1997.

(19) Sheldrick, G. M. *SHELXL97,* Program for Crystal Structure Refinement; University of Gottingen: Gottingen, Germany, 1997.

(20) Burnett, M. N.; Johnson, C. K.; *ORTEP-III,* Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations; Technical Report ORNL-6895 prepared for the Oak Ridge National Laboratory: Oak Ridge, TN, 1996.

(21) (a) Wells, A. F. *Structural Inorganic Chemistry,* 5th ed.; Clarendon Press: Oxford, U.K., 1984. (b) Bondi, A. *J. Chem. Phys.* **1964**, *41*, 3199.

(22) Tsuboyama, A.; Kuge, K.; Furugori, M.; Okada, S.; Hoshino, M.; Ueno, K. *Inorg. Chem.* **2007**, *46*, 1992.

(23) (a) Ray, L.; Shaikh, M. M.; Ghosh, P. *Inorg. Chem.* **2008**, *47*, 230. (b) Bisht, K. K.; Kathalikkattil, A. C.; Suresh, E. *RSC Adv.* **2012**, *2*, 8421.