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Article

Syntheses and Structures of Ag(I)-Containing Coordination Polymers and Co(II)-Containing Supramolecular Complex Based on Novel Fulvene Ligands

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Three new rigid conjugated fulvene ligands **L1**–**L3** were synthesized. **L1** and **L3** have been prepared by an aroylation reaction of cyclohexyl-substituted cyclopentadienyl anions. **L2** was prepared by the reaction of **L1** with $PhNHNH_2$ in hot enthanol. Six new coordination polymers, namely $[Ag(C_{25}H_{20}N_2O_2)(ClO_4)]\cdot 3.5C_6H_6$ (**1**), $[Ag_2(\mu\text{-}C_{31}H_{24}N_4)(\eta^2\text{-}C_6H_6)(H_2O)](ClO_4)_2\cdot(C_6H_6)\cdot(H_2O)_{0.5}$ (**3**), $[Ag(C_{31}H_{24}N_4)]SbF_6\cdot$solvate (**4**), $[Ag(C_{31}H_{24}N_4)](SbF_6)_2\cdot 2C_6H_6\cdot CH_2Cl_2$ (**5**), $[Ag(C_{25}H_{20}N_2O_2)_2]SbF_6$ (**6**), and $[Ag(C_{25}H_{20}N_2O_2)_2]SbF_6$ (**7**), and one seven-membered cobaltacycle-containing complex, namely $Co(C_{25}H_{20}N_2O_2)_2(C_2H_5OH)_2$ (**2**), were obtained through self-assembly based on these three new fulvene lignads. **L2**–**L3** and compounds **1**–**7** have been fully characterized by infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The results indicate that the coordination chemistry of new fulvene ligands is versatile. They can bind metal ions not only through the terminal N-donors and fulvene carbon atoms into organometallic coordination polymers but also through the two chelating carbonyl groups into unusual seven-membered metallo-ring supramolecular complexes. In the solid state, ligands **L1**–**L3** are luminescent. A blue-shift in the emission was observed between the free ligand **L1** and the one incorporated into Co(II)-containing complex **2**, and a red-shift in the emission was observed between the free ligand **L3** and the one incorporated into Ag(I)-containing polymeric compounds **6** and **7**.

Introduction

Self-assembly of organic ligands and inorganic metal ions is one of the most efficient and widely used approaches for the construction of supramolecular architectures.[1−3] Owing to their potential as new functional solid materials, interest in self-assembled coordination polymers with interesting physical properties has grown rapidly.[4] In this field, the coordination chemistry of bidentate or multidentate organodiamine ligands and polycyclic aromatic hydrocarbons ligands is the main theme. So far, a number of organic−inorganic coordination polymers based on organodiamine ligands[1a−b] (metal−heteroatom interaction) and organometallic coordination polymers based on polycyclic aromatic hydrocarbons[1c] (metal−carbon interaction) have been successfully synthesized. In contrast, the chemistry of supramolecular architectures based on fulvene molecules has received considerably less attention. It is well-known that fulvene is one of the most important classes of ligands in organometallic

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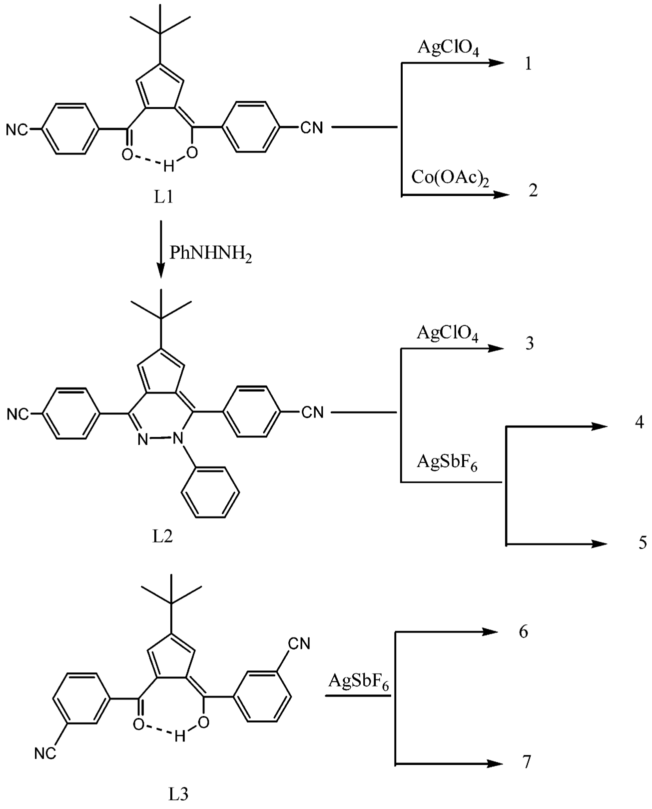
chemistry and widely utilized in synthesis of organometallic complexes based on metal−carbon interaction, such as metallocene. In our previous studies, we reported some new conjugated fulvene ligands, by the aroylation of substituted cyclopentadienyl anions, with both aromatic rings and −CN functional groups and several novel one-dimensional coordination polymers and supramolecular complexes based on them.[9] A −CN functional group on the aromatic ring, as we know, is a good candidate for coordination bonding as has been exploited in the self-assembly of Ag-supramolecular architectures. For example, a series of very attractive Ag-coordination polymers based on 1,3,5-tris(4-cyanophenylethynyl)benzene,[5] 4,4′-biphenyldicarbonitrile,[6] 3,3′-dicyanodiphenylacetylene,[7] and phenylacetylene nitriles with pendant oligo (ethylene oxide) side chains[8] has been reported by Moore and Lee. Fulvene together with −CN functional group would be a good candidate for synthesis of organometallic coordination polymers or supramolecular complexes based on both carbon−metal and heteroatom−metal interactions. This encouraged us to undertake further studies on fulvene ligands of this type and explore their interesting coordination chemistry. Following this approach, we now expand this chemistry with three new fulvene ligands (**L1**−**L3**). Six new Ag(I) coordination polymers, namely $[Ag(C_{25}H_{20}N_2O_2)(ClO_4)]\cdot 3.5C_6H_6$ (**1**), $[Ag_2(\mu\text{-}C_{31}H_{24}N_4)(\eta^2\text{-}C_6H_6)(H_2O)](ClO_4)_2\cdot(C_6H_6)\cdot(H_2O)_{0.5}$ (**3**), $[Ag(C_{31}H_{24}N_4)]SbF_6\cdot$unknown solvate (**4**), $[Ag(C_{31}H_{24}N_4)](SbF_6)_2\cdot 2C_6H_6\cdot CH_2Cl_2$ (**5**), $[Ag(C_{25}H_{20}N_2O_2)_2]SbF_6$ (**6**), and $[Ag(C_{25}H_{20}N_2O_2)_2]SbF_6$ (**7**), and one H-bonded Co(II) supramolecular complex, namely $Co(C_{25}H_{20}N_2O_2)_2(C_2H_5OH)_2$ (**2**), (Scheme1) were successfully isolated. In addition, luminescent properties of some of them were investigated in the solid state.

Scheme 1. Synthesis of Compounds **1**−**7**



Results and Discussion

Synthesis and Structural Analysis of Fulvene Ligands. Ligands **L1** and **L3** were prepared in moderate yield (61% for **L1** and 59% for **L3**) as deep-yellow crystalline solids by the reactions of 4-cyanobenzoyl chloride and 3-cyanobenzoyl chloride with *tert*-butyl-substituted cyclopentadienyl anions, which in turn were prepared from 6,6′-dimethylfulvene and CH_3Li in ether at 0 °C, respectively. **L2** was prepared in 80% yield as an orange crystalline solid by the reaction of **L1** with $PhNHNH_2$ in hot enthanol. In the ^1H NMR spectrum of **L1** and **L3**, a proton resonance was observed at 17.85 ppm as a singlet, which was attributed to the chelated proton, which is hydrogen bonded to the carbonyl next to the 1-aroyl group. The IR spectrum of **L1** and **L3** showed a −CN absorption band at 2250 cm^{-1}. It did not, however, show absorptions above 1630 cm^{-1} in the region normally assigned to organic carbonyl groups. The strong absorption band around 1620 cm^{-1} is, however, consistent with the hydrogen bonded enol structure, since it has been shown that conjugation and chelation lead to a large shift in the carbonyl infrared band.[10]

The structure of **L2** and **L3** were further confirmed by single-crystal X-ray diffraction. The crystal structure of **L3** reveals that the asymmetric unit contains two crystallographically and conformationally inequivalent molecules (**a**)

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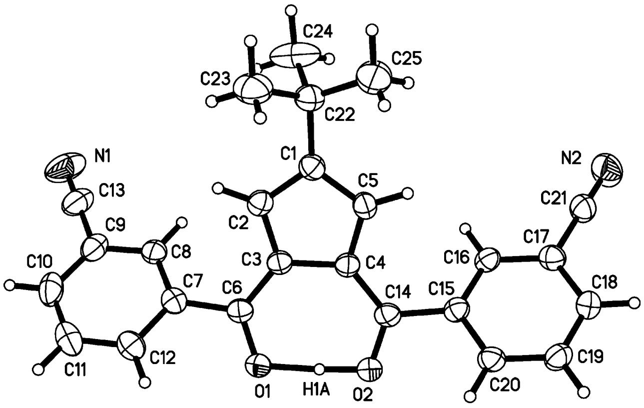

Figure 1. Molecular structure of **L3** (30% probability displacement ellipsoids).

and (**b**). For example in molecule (**a**), as shown in Figure 1, two aroyl groups on the tetracarbon-substituted cyclopetadienyl ring are adjacent. The C−C bond lengths on the substituted Cp-ring and also C(1)−C(5) and C(5)−C(14) range from 1.384 (2) to 1.420(2) Å, which is significantly shorter than a normal C−C single bond distance. Evidently, **L3** exists in the fulvene form.[10] The enol hydrogen atom (H(1)) is hydrogen bonded to the carbonyl oxygen atom (O(2), $d_{O(2)\cdots H(1)} = 1.34(2)$ Å, $\angle O(1)-H(1)\cdots O(2) = 177(2)°$, and $d_{O(1)\cdots O(2)} = 2.4379(17)$ Å) to provide a hydrogen bonded seven-membered ring. It is worth pointing out that the two $-C_6H_4-$CN-p rings and hydrogen bonded seven-membered ring are not in the same plane. The dihedral angles between $-C_6H_4-$CN-p rings and the hydrogen bonded seven-membered ring are 55.0(2)° and 52.3(2)°, respectively. The terminal (−CN) N···N separations in **L3** are 12.52 (cis conformation) and 14.67 (trans-conformation) Å, respectively. It is significantly longer than the terminal N···N separations of 7.122(4), 9.385(5), and 9.685(4) Å found in 4,4′-bipyridine,[11] *trans*-1,2-bis(4-pyridyl)ethene,[12] and 1,2-bis(4-pyridyl)ethyne,[13] respectively. There are two independent **L2** molecules (**a**) and (**b**) present in the asymmetric unit, too. For example in molecule (**a**), as shown in Figure 2, the hydrogen bonded seven-membered ring in **L1** was replaced by a six-membered phenyl-substituted pyridazine in **L2**. The contact between two terminal N-donors is 16.41(3) Å, which is slightly longer than the corresponding distances found in **L3**. In addition, **L2** could be considered as an angular ligand with a bite angle between one terminal −CN (N(4)) donor and one $N_{pyridazine}$ donor around 60°, which has a strong tendency to form cyclic moieties with inorganic metal ions.[13c] Such a kind of geometric configuration together with the other terminal N-donor would be expected to form metallacycle-containing coordination polymers or supramolecular complexes.

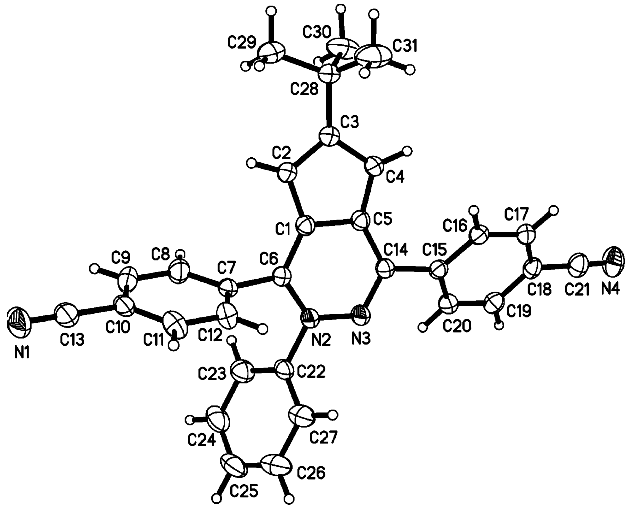

Figure 2. Molecular structure of **L2** (30% probability displacement ellipsoids).

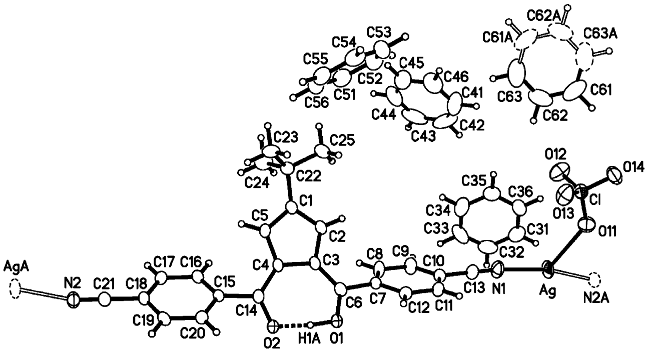

Figure 3. ORTEP figure of compound **1** with 30% probability ellipsoids.

Synthesis and Structural Analysis of 1. Reaction of **L1** with $AgClO_4 \cdot xH_2O$ (1:2 ratio) in benzene at room temperature afforded compound **1** as orange cubic crystals in 54% yield. Compound **1** loses guest solvent molecules quickly and is not stable outside of the mother liquor. Single-crystal analysis revealed, as shown in Figure 3, compound **1** crystallizes in the triclinic system $P\bar{1}$. The asymmetric unit consists of one Ag(I) center, one **L1** ligand, one ClO_4^- counterion, three full benzene molecules of crystallization, and another half-benzene located on an inversion center. Ag(I) center adopts a $\{AgN_2O\}$ (Ag−N(1) = 2.139(2), Ag(1)−N(2)#1 = 2.169(2), Ag(1)−O(11) = 2.5463(19) Å) coordination sphere, which is commonly observed in Ag(I) complexes. In addition, one guest benzene molecule is located close to the Ag(I) metal center. The shortest Ag(I)···C contact (Ag···C(31)) is only 3.070(3) Å, which is beyond the bond length limits (2.47 to 2.80 Å) commonly observed in Ag(I) aromatic complexes.[14]

In the solid state, Ag(I) metal centers are connected to each other by bidentate ligands **L1** through the terminal −CN nitrogen atoms into a one-dimensional linear chain extended

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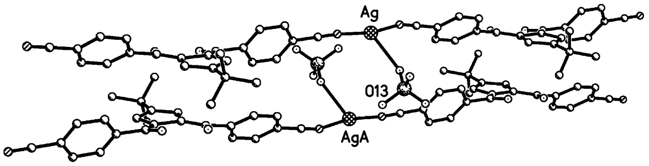

Figure 4. One-dimensional double chain in **1**.

along crystallographic [11$\bar{1}$] direction. The intrachain Ag···Ag separation is 21.00(3) Å. As shown in Figure 4, weakly coordinated ClO_4^- counterions are located between these one-dimensional chains and, moreover, they link these one-dimensional polymer chains into a double chain motif via weak inter-polymer Ag(I)−O interactions. The corresponding Ag−O (Ag(1)−O(13)) bond distance is 2.742(3) Å.[1b]

The shortest interchain Ag···Ag separation is 4.80(4) Å, which is longer than the sum of the van der Waals radii of two silver atoms, 3.44 Å.[15] In addition, $\pi-\pi$ interactions[16] are present in **1** (Figure 5). Chain pairs are linked into two-dimensional layers through $\pi-\pi$ interactions of {C15···C20}−{C15*···C20*} across an inversion center ($d_{\text{centroid-centroid}}$ = 3.599 Å). As shown in Figure 6, benzene guest molecules are located between layers and give rise to an interesting ordered arrangement due to their edge-to-face interactions commonly observed in the crystal structure of benzene (Figure 7).[17] The shortest intermolecular C−C separation is 3.472 Å, which is similar to those reported for related compounds, such as pyrene and 1-propynylpyrene.[18]

Synthesis and Structural Analysis of 2. As shown in Figure 1, fulvene ligands of this type have not only terminal −CN coordination sites but also *cis*-1,4-diketone moiety. The specific geometry herein affords a scarce opportunity to synthesize seven-membered metallo-ring complexes that are not achievable easily by other kinds of 1,4-diketone-type ligands. The complex **2** was synthesized by reaction between **L1** and $Co(OAc)_2 \cdot 2H_2O$ in hot ethanol. When a solution of **L1** in ethanol was treated with $Co(OAc)_2 \cdot 2H_2O$, in a metal-to-ligand molar ratio of 1:2, compound **2** was obtained as the neutral molecular compound with seven-membered metallo-rings. It is worth pointing out that the coordination chemistry of **L1** with transition metal templates Co(II) are independent of the metal-to-ligand mole ratio. For example, when the metal-to-ligands ratio changed from 1:1 to 2:1, even 3:1, the compound **2** is always isolated as the only product. Compound **2** crystallizes in the triclinic system. As shown in Figure 8, Co(II) center lies in an octahedral coordination environment defined by four O-donors from two bidentate ligands **L1** and two O-donors from two coordinated ethanol solvent molecules. The octahedral coordination polyhedron is slightly distorted, where all angles around the copper center deviate significantly from 90° (O(1)−Co−O(2) = 91.32(7)°, O(1)−Co−O(3) = 95.29(9)°, O(2)−Co−O(3) = 90.82(9)°). The Co−O bond distances on the basal plane are 2.0022(16) and 2.0052(16) Å, respectively, which compare well with the Co−O distances found in cobalt−oxygen complexes.[19] The distances between the cobalt center and the two axial O-donor atoms are the same ($d_{\text{Co-O}}$ = 2.137(3) Å), again consistent with corresponding bond lengths in those complexes with similar coordination envoronment.[19] It is well-known that neutral or deprotonated 1,2-diketone or 1,3-diketone compounds can be the chelating ligands to bind transition metal ions into five- or six-membered metallo-ring systems which engender less strain,[20a] because the atoms on the rings are allowed to adopt more closely their natural bond angles. It is much less known that seven-membered metallo-ring complexes can be generated from neutral or deprotonated 1,4-diketone-containing ligands and transition metal ions probably due to the conformational strain effect.[20a] However, some interesting seven-membered metallacycle complexes were reported recently, such as metal complexes generated from TADDOL,[20b] diazoacetate,[20c] bis(phosphane) ligands,[20d] and related bidentate chelating ligands.[20e] Some of them are demonstrated to be very useful catalysts in metal-catalyzed stereoselective syntheses. Owing to its specific molecular geometry, ligand **L1** reported herein presents an additional perfect example for the synthesis of seven-membered metallo-ring transition metal complexes. The four −CN groups in **2** are uncoordinated and every two of them aligned along the same axis, but are oriented in the reverse directions. The IR spectrum of **2** shows that the −C≡N stretch (2255 cm^{-1}) was essentially unchanged from free ligand **L1**, which can be taken as evidence for the nitrile nitrogen not entering the coordination sphere of the Co(II) center. A similar phenomenon occurs in the reaction of Ru_2-

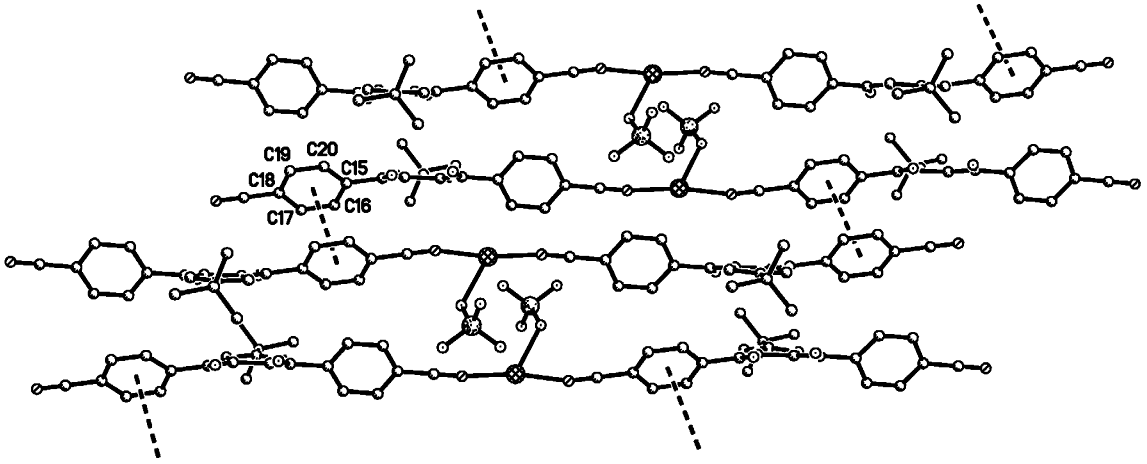

Figure 5. Two one-dimensional double chains linked by $\pi-\pi$ interactions.

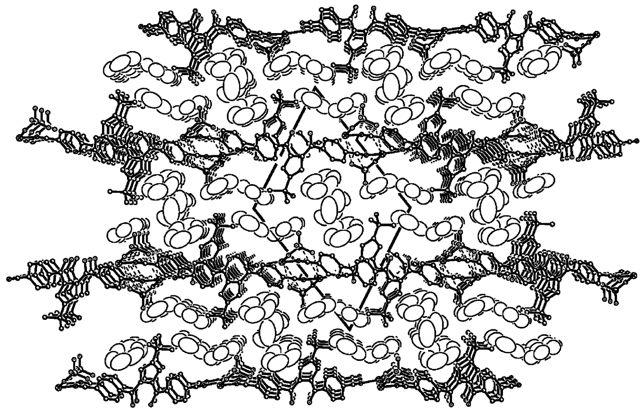

Figure 6. Crystal packing of **1**.

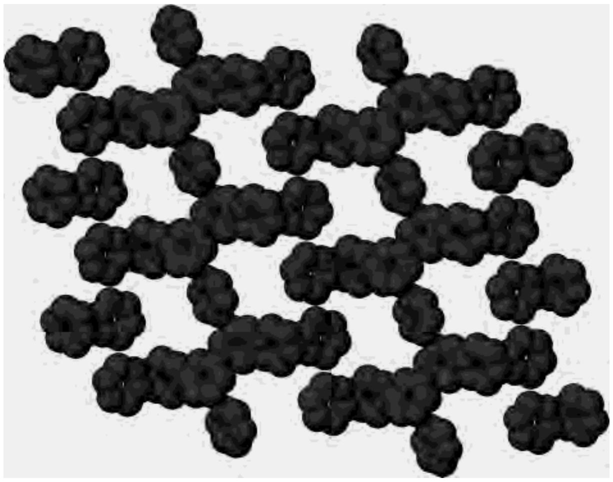

Figure 7. Edge-to-face arrangement of benzene guest molecules in **1**.

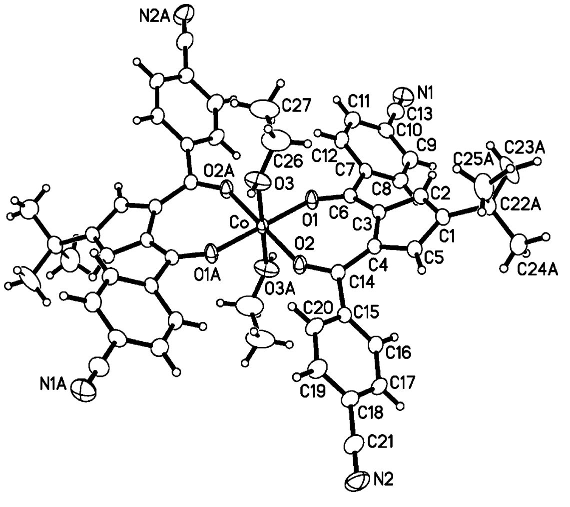

Figure 8. ORTEP figure of compound **1** with 30% probability ellipsoids.

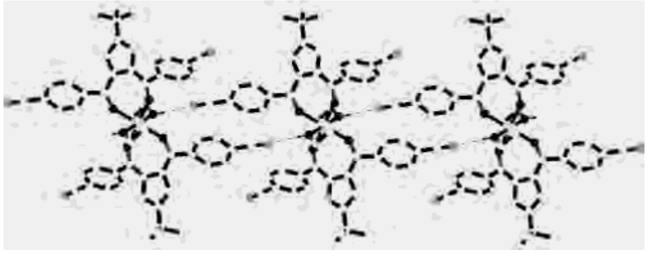

Figure 9. Hydrogen-bonded one-dimensional chain motif found in compound **2**. Hydrogen bonds are shown as thin lines.

$(O_2C(CH_2)_6CH_3)_4$ in toluene and $Cu(hfacac)_2 \cdot H_2O$ (hfacac = hexafluoroacetylacetonate) in methylene chloride with 4-cyanopyridine and 3-cyanopyridine, respectively.[21] The discrete molecular 1:2 adduct $Ru_2(O_2C(CH_2)_6CH_3)_4$(4-cyanopyridine)$_2$ and $Cu(hfacac)_2$(3-cyanopyridine)$_2$ are obtained instead of the expected 4-cyanopyridine and 3-cyanopyridine bridged transition metal complexes. It is known that 4-cyanopyridine and 3-cyanopyridine spacers have been used as bridging ligands to link transition metal species into dimers and polymers.[22,23] It appears that the nitrile N-donor atom has a poor coordinating ability to effectively link 3d metal ions. For example, in [(Cu(4-cyanopyridine)$_4$(H_2O)(ClO_4)$_2$)$_n$, the nitrile nitrogen only weakly coordinates with copper centers through a "semi-coordinated" bond ($Cu{-}N{\equiv}C$ is 2.649(4) Å), which is much longer than a normal Cu−N coordinative bond.[24] It is worth noting that **2** contains uncoordinated N-donors, and could be used as a potential new metal-containing building block, as suggested recently.[25] These building blocks could be connected by other suitable metal ions (Ag^+ or Cd^{2+}, for example) or unsaturated metal complexes via bonding interactions with the free nitrile nitrogen atoms in **2**, a direction we are pursuing. The shortest Co···Co distance is 12.66(3) Å.

In the solid state, as shown in Figure 9, the neutral building blocks of **2** arrange parallel to the crystallographic *c* axis, and moreover are bound together by strong intermolecular N···O−H hydrogen bonds in a hand-in-hand fashion to create a one-dimensional chain motif along crystallographic *b* axis. The hydrogen bonding system in **2** consists of the one uncoordinated nitrogen atom N(1) on −CN group with the hydrogen atom H(3A) on the coordinated ethanol molecule O(3) of a neighboring Co(II) complex. The N(1)···H(3)

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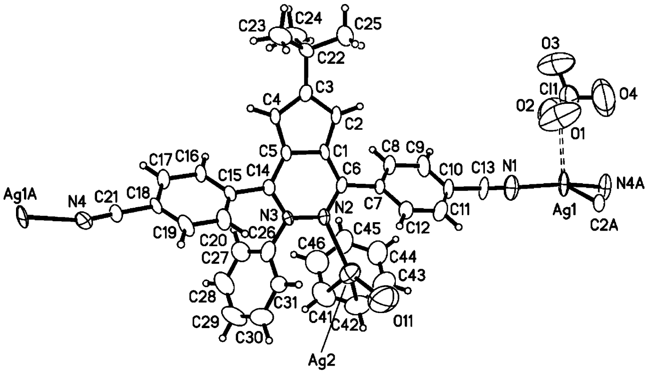

Figure 10. Molecular structure of **3**.

distance is 2.18(2) Å. The corresponding O(3)···N(1) distance is 2.909(3) Å, and the corresponding O(3)−H(3)···N(1) angle is 173(4)°. The existence and structural importance of strong hydrogen-bonding interactions generated from −CN (as the hydrogen bond acceptor) are now well established and observed in many compounds.[26] It is no doubt that these strong hydrogen bonding interactions contribute significantly to the alignment of the molecules of **2** in the crystalline state.

Synthesis and Structural Analysis of 3. Compound **3** was obtained as red-orange crystals by combination of **L2** with $Ag(ClO_4)\cdot xH_2O$ in CH_2Cl_2/C_6H_6 mixed solvent system. Crystals of **3** lose solvent molecules and turn opaque within several minutes under ambient atmosphere. Single-crystal analysis revealed, as shown in Figure 10, that there are two different Ag(I) centers in **3**. The coordination sphere around the first silver atom is distorted tetrahedral, being made of two N-donors (N(1) and N(2)) from two ligands **L2** (Ag−N(1) = 2.166(10) and Ag−N(2) = 2.165(10) Å), one O-donor (O(1)) from ClO_4^- counterion (Ag−O(1) = 2.6122(2) Å),[27] and one carbon atom (C(2)) from the substituted Cp group on the third ligand **L2.** The Ag−C distance is 2.679(9) Å, while the remaining Ag−C contacts are greater than 2.80 Å which is beyond the limits (2.47 to 2.80 Å) commonly observed in Ag(I)−aromatic complexes.[14] Thus, the substituted five-membered ring in **L2** coordinates to the Ag(I) ion with an η^1 bonding mode, which is normally observed in arene−silver complexes.[28] The second Ag(2) center adopts a $\{AgC_2NO\}$ oragnometallic pseudotetrahedral coordination environment, which consists of two carbon atoms (C(41) and C(42)) from solvent benzene molecule, one aquo oxygen atom (Ag(2)−O(11) = 2.290(13) Å), and one nitrogen donor (N(2)) from six-membered phenyl-substituted pyridazine moiety (Ag(2)−N(2) = 2.317(8) Å). For the Ag(2) center, the two $Ag-C_{benzene}$ bond distances (2.444(16)−2.571(15) Å) lie in the range of normal Ag−C bond distances 2.47−2.76 Å, while the remaining Ag−C contacts are greater than 2.86 Å, which is beyond the limits commonly observed in Ag(I)−aromatic complexes.[14] Thus, the benzene ring in **1** coordinates to the Ag(I) ion with an η^2 instead of an η^1 bonding mode, which is normally observed in arene−silver complexes.[28]

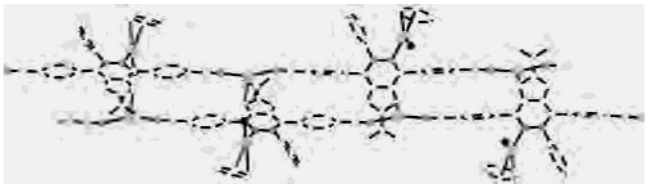

Figure 11. One-dimensional organometallic ladder-like chain in **3**.

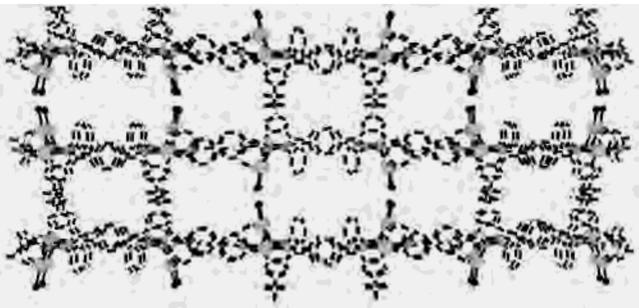

Figure 12. Crystal packing of **3**. Benzene and water solvent molecules and ClO_4^- counterions are omitted for clarity.

In the solid state, as shown in Figure 11, Ag(2) centers are connected to each other by **L2** ligands through two terminal N-donors into one-dimensional chains along the crystallographic *a* axis. The shortest intrachain Ag(2)...Ag(2) distance is 20.85(4) Å. These one-dimensional chains are further linked together by five-membered ring-Ag(2) (C(2)−Ag(1)) linkages into an interesting ladder-like motif.[29] The Ag(I)−benzene moieties are located outside the ladder and bound to it through $Ag(1)-N_{pyridazine}$ bond interaction. The shortest intrachain Ag(1)···Ag(1) distance is 20.56(4) Å. These chains stack together along the crystallographic *b* axis and generate channels along the crystallographic *c* axis. The benzene and water solvent molecules and ClO_4^- counterions are located in the channels as the guest (Figure 12). To date, a number of Ag(I)-containing coordination polymers have been successfully generated from inorganic silver salts and various types of rigid and flexible organic spacers based on Ag−heteroatom[1a−b] or Ag−π interactions,[1c,3 g] respectively. To our knowledge, silver coordination polymers or supramolecular networks based on both metal-heteroatom and metal−carbon interactions are still unusual, especially for Cp-metal-containing ones.[9d] Fulvene organic spacers reported herein are good candidates for preparation of Cp-Ag(I) moiety-containing organometallic coordination polymers or supramolecular complexes.

Synthesis and Structural Analysis of 4 and 5. When a solution of **L2** in CH_2Cl_2 was treated with $AgSbF_6$ in benzene, compounds **4** and **5** were obtained successively as yellow and red crystals, respectively. Compounds **4** and **5** are not air stable. As shown in Figure 13, compound **4** crystallizes in the tetragonal system with the space group *P*4/*n*. The asymmetric unit consists of the Ag(I) center, one **L2** ligand, and an SbF_6^- anion disordered over two closely

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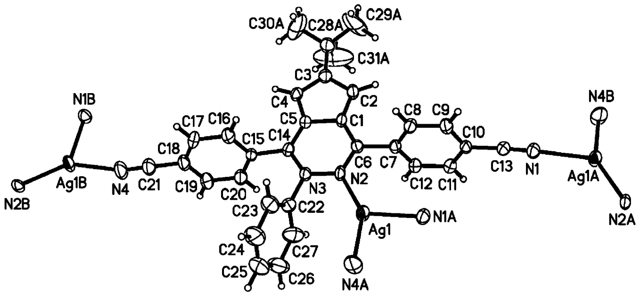

Figure 13. ORTEP figure of compound **4** with 30% probability ellipsoids.

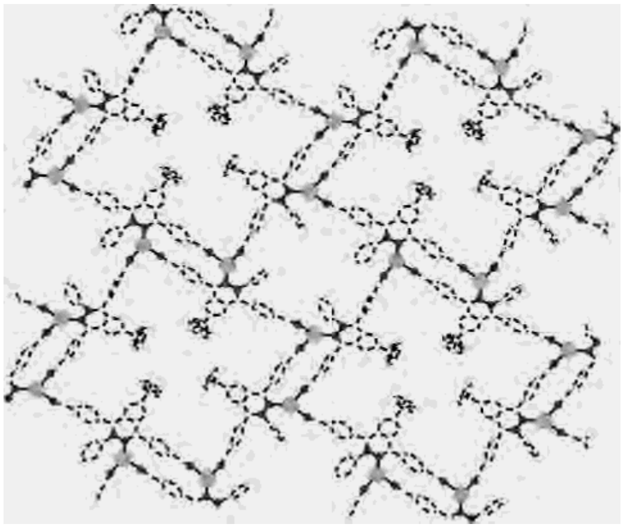

Figure 14. Two-dimensional net in **4**.

spaced positions. The final occupancy values are 0.925/0.075. The Ag(I) centers in **4** lie in a distorted trigonal coordination environment[4f] which consists of two terminal CN-donors (Ag(1)−N(1)#2 = 2.327(4) and Ag(1)−N(4)#1 = 2.203(5) Å) from two **L2** ligands and one phenyl-substituted pyridazine nitrogen donor (N(2), Ag(1)−N(2) = 2.199(4) Å) from the third **L2** ligand.

In the solid state, as shown in Figure 14, **L2** ligands bind Ag(I) centers through one pyridazine nitrogen donor (N(2)) and one terminal nitrile N-donor (N(1)) into a binuclear metallacycle. These binuclear metallacycles are further linked together by the other terminal nitrile N-donor (N(1)) into a novel two-dimensional net extended in crystallographic *ab* plane. It is worth pointing out that this two-dimensional net consists of three different kinds of metallacyacles, i.e., big square-like quadrinuclear, medium square-like quadrinuclear, and small rectangle-like binuclear metallacycles. Their crystallographic square-grid dimensions[30] are 20.83 × 20.83 and 12.37 × 12.37 Å, respectively, and the rectangle-grid dimension is 9.15 × 3.14 Å. These two-dimensional sheets stack together in ABAB fashion along crystallographic *c* axis to generate a noninterpenetrating square-channels containing network. It is well-known that interpenetrating square-grid polymers are typically nonporous since all available spaces are filled by the interpenetration; even large noninterpenetrating square-grid coordination polymers, such as **4**, can have reduced porosity due to the stacking of the nets. In the case of **4** the ABAB stacking of the layers generates reduced, yet still large, infinite channels of dimensions of 12.36 × 12.36 Å (Figure 15). The solvent-accessible region calculated with the PLATON program[31] is 654.1 Å^3 or 10.0% of the total unit cell volume. A series of binuclear metallacycle-containing polymeric compounds were reported recently,[13c] wherein those Cd(II)-metallacyclic building blocks are connected to each other through coordinated NO_3^- counterions into extended structures. Compared to 2,4′-bipyrindyl type ligands,[13c] **L2** is more suitable to generate binuclear, even multinuclear, metallacyclic polymeric complexes.

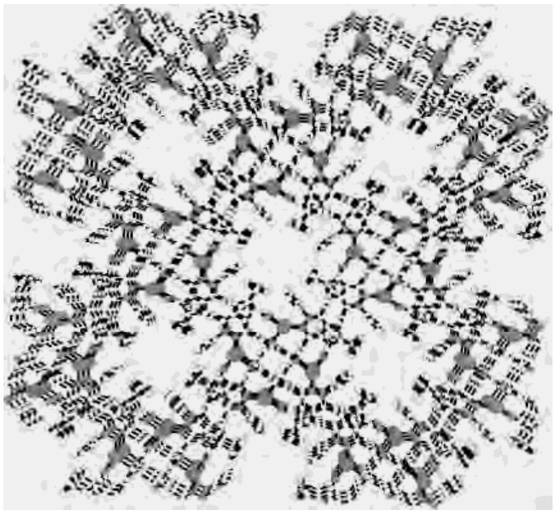

Figure 15. Crystal packing of **4**.

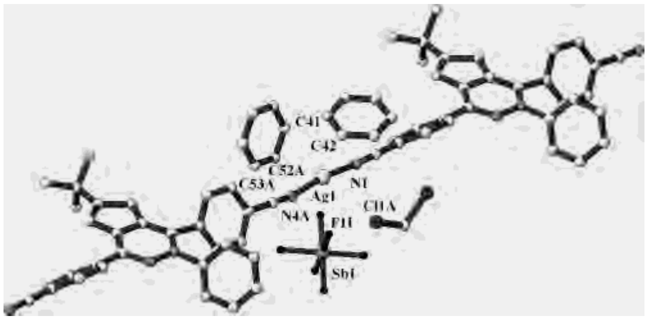

Figure 16. Molecular structure of **5**.

Compound **5** was obtained as red crystals at only 9% yield. Single-crystal analysis revealed that **5** crystallizes in the monoclinic space group $P2_1/c$. All species reside on positions of general crystallographic symmetry. The *tert*-butyl substituent of the **L2** ligand is rotationally disordered over two orientations, and was refined with the aid of 10 C−C same-distance restraints. Occupancies for each disorder component were initially refined but subsequently fixed near the final refined values (0.65/0.35) for stability. As shown in Figure 16, Ag(I) center adopts a linear coordination environment which consists of two terminal nitrile N-donors from two

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(30) The pore dimensions described here are crystallographic scalar quantities, and do not account for the van der Waals radii of the atoms defining the pore.

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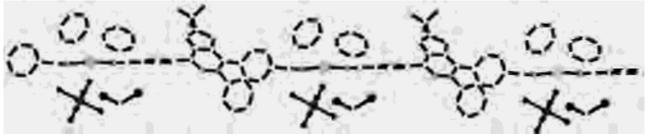

Figure 17. One-dimensional chain found in **5**.

L2 ligands (N(1)−Ag(1)−N(4)#1 = 172.4(2)°, Ag(1)−N(1) = 2.123(5) Å, and Ag(1)−N(4)#1 = 2.147(5) Å). In addition, there are two benzene and one methylene chloride solvent molecules for every Ag atom and they are located very close to the Ag(I) centers (Ag(1)−Cl(1A) = 3.397(2), Ag(1)−C(41) = 3.002(7), Ag(1)−C(42) = 3.018(7), Ag1−C(52A) = 3.204(7), and Ag(1)−C(53A) = 3.283(7) Å). The SbF_6^- counterion coordinates to Ag(I) center very weakly with the shortest Ag···F contact 2.705(5) Å. [32] Phenyl-substituted pyridazine nitrogen donor is not involved in the Ag(I) coordination sphere, which is quite different from that of compound **4**. In the solid state, as shown in Figure 17, Ag(I) centers are bound together by **L2** ligands into a one-dimensional chain along the [101] crystallographic direction. The intrachain Ag(I)···Ag(I) distance is 20.61(7) Å. It is worth pointing out that the two substituted benzonitriles show a dihedral angle of 100.4° whereas ones in free **L2** ligand are slightly twisted, showing a dihedral angle of 23°. Those uncoordinated SbF_6^- counterions and solvent molecules are located between chains.

Synthesis and Structural Analysis of 6. The idea behind the use of ligand **L3** is to control supramolecular motifs through 3,3′-dicyano-type ligands.[33] It is well-known that the relative different orientations of the nitrogen donors and also the different bridging spacing might result in unusual building blocks, and then lead to the construction of supramolecular motifs which have not been achieved using normal rigid linear bidentate organic ligands. We earlier reported a series of novel coordination polymers generated from rigid bidentate 4,4′-bipyridine- and 3,3′-bipyridine-type Schiff-base ligands.[34] Indeed, our previous studies demonstrated that the relative different orientation of the coordinating sites is one of the most important factors to control the polymeric motifs. Compound **6** was obtained as orange crystals by combination of **L3** and $AgSbF_6$ in a benzene and methylene chloride mixed solvent system at 37% yield. Single-crystal X-ray analysis revealed that **6** crystallizes in the triclinic crystal system in the space group $P\bar{1}$. The asymmetric unit contains two independent ligands per Ag(I) atom and SbF_6^- unit. The Ag(I) center lies in a distorted tetrahedral coordination sphere which consist of four N-donors (Ag−N(3)#1 = 2.294(4), Ag−N(4) = 2.301(4), Ag−N(2)#2 = 2.316(4), and Ag−N(1) = 2.338(4) Å) from four **L3** ligands (Figure 18).

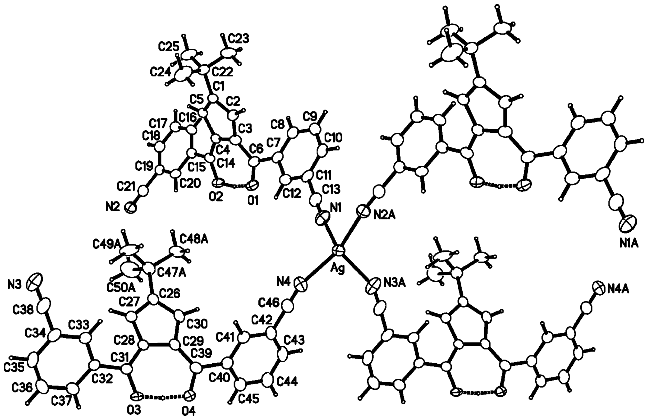

Figure 18. ORTEP figure of compound **6** with 30% probability ellipsoids.

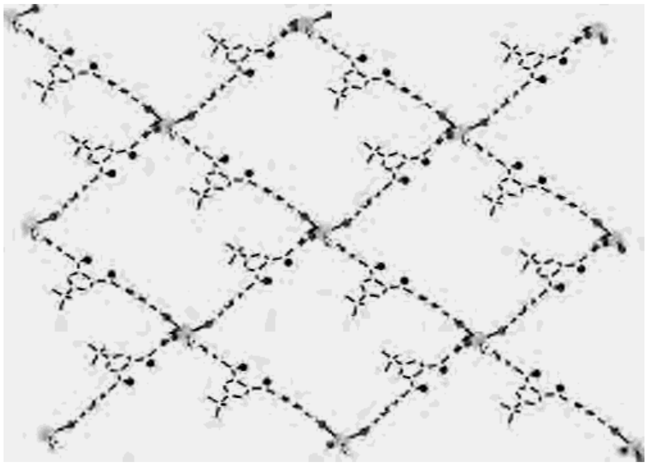

Figure 19. View perpendicular to one 2-D layer.

In the solid state, distorted tetrahedral Ag(I) centers are connected to each other by two crystallographically independent **L3** ligands through the phenyl-CN groups into infinite two-dimensional square sheets parallel to the crystallographic [001] plane. It is worth pointing out that **L3** ligands, as noted above, adopt cis conformation to coordinate Ag(I) centers in **6**. Cis conformation orients the two −CN groups in the same direction, and would allow them to bind at the neighboring metal center in the two-dimensional net. As shown in Figure 19, each square unit consists of four Ag(I) atoms and four **L3** ligands—in fact, it is a 64-membered ring structure (Figure 19). The effective cross section of ca. 16 × 16 Å,[30] which is significantly larger than those related compounds generated from 4,4′-bipyridine and transition metals (M = Cd, Zn, Ni, Cu) with the similar square pattern (the square dimension is ca. 8 × 8 Å).[35] There are two sets of such two-dimensional sheets in **6** and they interpenetrate together to form a layer with SbF_6^- anions stuffed in. These interpenetrated layers stack upon one another along [001].

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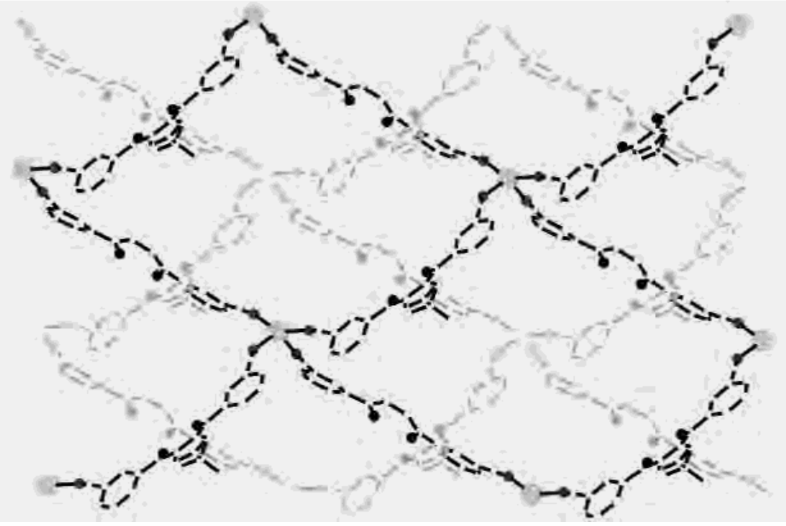

Figure 20. Each layer made up of two interpenetrated sheets.

The *tert*-butyl group from one interpenetrated double layer stick into the adjacent double layer—interdigitation. When viewed down the crystallographic *c* axis, the Ag(I) centers in one set occupy the center of the channels formed by the other sets (Figure 20). Such interpenetration effectively reduces the volume of the cavities and channels and no guest molecules are found in **6**.

Synthesis and Structural Analysis of 7. It is worth pointing out that the coordination chemistry of **L3** with Ag(I) metal template appears to be quite versatile, with the products dependent on the choice of solvent system, and largely independent of the metal-to-ligand mole ratio. However, increasing the ligand-to-metal ratio resulted in somewhat higher yield and higher crystal quality. When a solution of **L3** in the nonpolar solvent benzene was treated with $AgSbF_6$ in the same solvent with the same metal-to-ligand mole ratio, the only product yielded was $[Ag(C_{25}H_{20}N_2O_2)_2]SbF_6$ (**7**), which crystallizes with a novel three-dimensional diamondoid motif distinctly different from the polymeric motifs found in compound **6**. In other words, the proper selection of solvent system and template ions in the synthetic process is critical in directing the self-assembly of coordination polymers, an observation which has been borne out by many previous studies.[36] Single-crystal X-ray analysis revealed that **7** crystallizes in the monoclinic crystal system in the space group *C*2/*c*. As shown in Figure 21, the Ag(I) metal ion in **7** lies in a distorted tetrahedral coordination environment defined by four N-donors from four **L3** ligands. For **7**, the Ag−N bond lengths range from 2.253(4) to 2.410(4) Å, which are well comparable with bond lengths found in **6**.

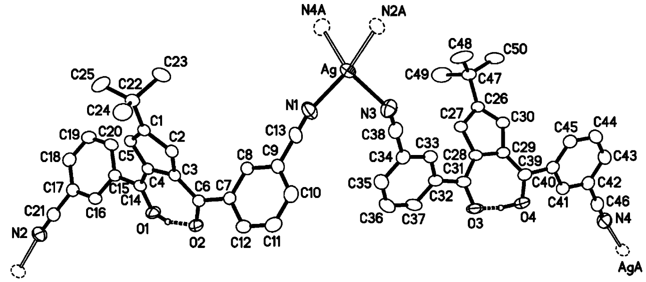

Figure 21. ORTEP figure of compound **7** with 30% probability ellipsoids.

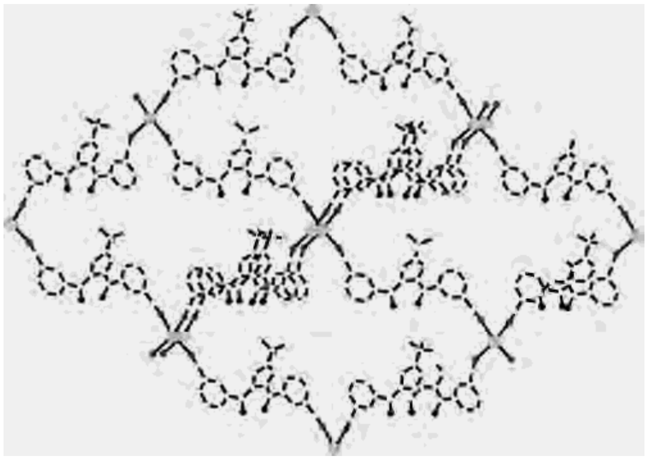

Figure 22. One independent framework shown of **7**.

In the solid state, Ag(I) centers are connected to each other by **L3** ligands into a three-dimensional diamondoid structure (Figure 22).[1b] It is noteworthy that two independent frameworks interpenetrate to produce channels occupied by SbF_6^- counterions. In addition, **L3** ligand adopts transoid conformation to coordinate Ag(I) centers in **7**, which is different from that in **6**. *Trans*-conformation orients the two −CN groups in two different directions, and allows them to bind metal centers into higher dimensional framework. It is well-known that the diamondoid structure is the motif that can be observed for three-dimensional structures based on tetrahedral building blocks. Several polymeric complexes

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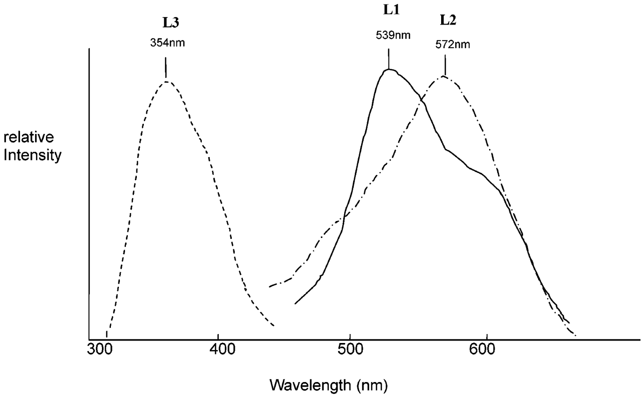

Figure 23. Photoinduced emission spectra of **L1**−**L3** in the solid state at room temperature.

such as Cu(bpe)$_2$BF$_4$,[37] Cu(bpy)$_2$PF$_6$,[38] Ag(bpy)CF$_3$SO$_3$,[39] and Cu(dzp)$_2$PF$_6$[40] were reported and their interpenetration reduced from 5-fold to 3-fold, which suggests that the steric bulk of the ligands could prevent the interpenetration effectively. The steric influence of big substituted groups on **L3** could be the reason that compound **7** reported herein exhibits only 2-fold interpenetrating diamondoid motif.

Luminescent Properties. Aromatic organic molecules, all-organic polymers, and mixed inorganic−organic hybrid coordination polymers have been investigated for fluorescence properties and for potential applications as light-emitting diodes (LEDs).[41] Owing to the ability of affecting the emission wavelength of organic materials, syntheses of inorganic−organic coordination polymers by the judicious choice of organic spacers and transition metal centers can be an efficient method for obtaining new types of electroluminescent materials.[42] The luminescent properties of free ligands **L1**−**L3**, and their metal complexes **2**, **6**, and **7**, were investigated in the solid state. The spectra of **L1**−**L3** in solid state are shown in Figure 23. **L1**, **L2**, and **L3** exhibit one emission maximum at 539, 572, and 354 nm, respectively. The emission band of Co(II)-containing complex **2** is blue-shifted to 532 nm compared to the emission color of **L1**, however, the emission bands of Ag(I)-containing polymeric compounds **6** and **7** are red-shifted to 533 and 531 nm, respectively (Figure 24). No enhancement of the fluorescence intensity is realized. Because of their instability, the luminescent properties of **1** and **3**−**5** could not be investigated. The emission colors of free **L1** and **L3** were significantly affected by its incorporation into the M-containing (M = Co(II) and Ag(I)) complexes, as evidenced by the large shift in the emission.

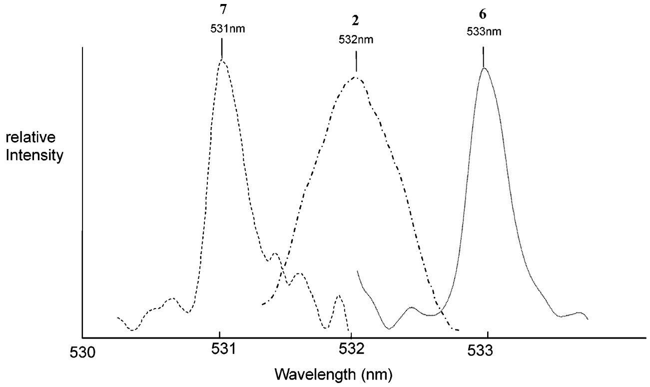

Figure 24. Photoinduced emission spectra of **2**, **6**, and **7** in the solid state at room temperature.

Conclusions

Three new fulvene ligands were synthesized. **L1** and **L3** were synthesized by an aroylation reaction of cyclohexyl-substituted cyclopentadienyl anions. **L2** was prepared by the reaction of **L1** with PhNHNH$_2$ in hot enthanol. The coordination chemistry of **L1**−**L3** were investigated systemically. The results indicate that the coordination chemistry of new fulvene ligands is versatile. They can bind metal centers not only through the terminal N-donors and fulvene carbon atoms into organometallic coordination polymers but also through the two chelating carbonyl groups into unusual seven-membered metallo-ring supramolecular complexes. In the solid state, ligands **L1**−**L3** are luminescent. A blue-shift in the emission was observed between the free ligand **L1** and the one incorporated into Co(II)-containing complex **2**, and a red-shift in the emission was observed between the free ligand **L3** and the one incorporated into Ag(I)-containing polymeric compounds **6** and **7**. We are currently extending this result by preparing additional fulvene-type ligands of this kind that have different substituted organic functional groups. We anticipate this approach to be useful for the construction of a variety of new transition metal complexes and luminescent coordination polymers with novel structures that have the potential of leading to new fluorescent materials.

Experimental Section

Materials and Methods. 4-Cyanobenzoyl chloride, 3-cyanobenzoyl chloride, 6,6′-dimethylenefulvene, and CH$_3$Li were prepared according to literature methods. Inorganic metal salts were purchased from Acros and used without further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400−4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^{1}H NMR data were collected using a JEOL FX 90Q NMR spectrometer. Chemical shifts are reported in δ relative to TMS. Element analyses were performed on a Perkin-Elmer model 240C analyzer.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Synthesis. Preparation of L1. A solution of 4-cyanobenzoyl chloride (2.00 g, 12.5 mmol) in anhydrous ether (20 mL) was added dropwise to a solution of *tert*-butyl-substituted cyclopentadienyl anions (16.2 mmol) in anhydrous ether at 0 °C, which derived from 6,6′-dimethylenefulvene (18.8 mmol) and CH$_3$Li (18.8 mmol) in

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Table 1. Crystallographic Data for **L2**, **L3**, and **1**−**3**

	$C_{32}H_{27}N_4O_{0.50}$	$C_{25}H_{20}N_2O_2$	$C_{46}H_{41}AgClN_2O_6$	$C_{54}H_{50}CoN_4O_6$	$C_{43}H_{39}Ag_2Cl_2N_4O_{9.5}$
formula	**L2**	**L3**	**1**	**2**	**3**
formula weight	475.58	380.43	861.13	909.91	1050.42
crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	11.3927(6)	9.7027(9)	10.3433(5)	7.8699(5)	42.289(3)
b (Å)	29.4124(16)	12.8883(12)	14.3521(7)	12.6649(8)	18.2148(13)
c (Å)	15.7412(9)	16.8118(16)	15.5484(8)	12.8184(8)	11.1327(8)
α (deg)	90	74.200(2)	65.4250(10)	92.5710(10)	90
β (deg)	105.5330(10)	89.116(2)	87.3260(10)	98.2910(10)	103.677(2)
γ (deg)	90	84.894(2)	72.9880(10)	106.9780(10)	90
V (Å^3)	5082.0(5)	2014.8(3)	1999.72(17)	1204.06(13)	8332.3(10)
Z	8	4	2	1	8
ρ calc (g/cm^3)	1.243	1.254	1.430	1.255	1.675
μ (mm^{-1})	0.075	0.080	0.623	0.410	1.131
temperature (K)	150(1)	150(1)	150(1)	294(1)	150(1)
no. refl.	10421	7122	8179	4271	6639
R1; wR2 ($I > 2\Sigma(I)$)	0.0586; 0.1600	0.0496; 0.1158	0.0391; 0.0831	0.0492; 0.1200	0.0979; 0.2516

Table 2. Crystallographic Data for **4**−**7**

	$C_{31}H_{24}AgF_6N_4Sb$	$C_{44}H_{38}AgCl_2F_{12}N_4Sb_2$	$C_{50}H_{40}AgF_6N_4O_4Sb$	$C_{50}H_{40}AgF_6N_4O_4Sb$
formula	**4**	**5**	**6**	**7**
formula weight	796.16	1273.05	1104.48	1104.48
crystal system	Tetragonal	Monoclinic	triclinic	Monoclinic
space group	$P4/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
a (Å)	26.2633(7)	19.3530(9)	8.9189(4)	34.7405(19)
b (Å)	26.2633(7)	15.0315(7)	13.5085(6)	9.1035(5)
c (Å)	9.3983(5)	17.8900(8)	19.1073(9)	31.9219(18)
α (deg)	90	90	86.3540(10)	90
β (deg)	90	112.9510(10)	85.0180(10)	111.2640(10)
γ (deg)	90	90	84.0390(10)	90
V (Å^3)	6482.6(4)	4792.3(4)	2277.51(18)	9408.3(9)
Z	8	4	2	8
ρ calc (g/cm^3)	1.632	1.430	1.611	1.560
μ (mm^{-1})	1.498	1.718	1.097	1.063
temperature (K)	150(1)	150(1)	150(1)	293(2)
no. refl.	5171	8462	8004	8372
R1; wR2 ($I > 2\Sigma(I)$)	0.0479; 0.1262	0.0536; 0.1255	0.0474; 0.0870	0.0435; 0.1176

anhydrous ether. The mixture was stirred overnight at room temperature. The solvent was then reduced to about 10 mL under vacuum. Hexane was added and an orange solid precipitated. The solid was washed with hexane several times and stirred in HCl (5% in water) overnight. The final product was purified by column chromatography on silica gel (CH_2Cl_2/hexane, 2:1) to afford an orange crystalline solid (1.45 g, 61%). IR (KBr pellet) ν (cm^{-1}) = 3140 (s), 2970 (s), 2880 (s), 2250 (vs), 1620 (vs), 1600 (vs), 1510 (vs), 1410 (vs), 1365 (s), 1350 (s), 1180 (s), 1110 (s), 1015 (s), 940 (s), 845 (s), 745 (s). ^{1}H NMR (90 MHz, $CDCl_3$, 25 °C, TMS): δ = 17.85 (s, 1H, −OH), 7.84 (s, 8H, $-C_6H_4$), 7.07 (s, 2H, $-C_5H_2$), 1.21 (s, 9H, $-CH_3$). Elemental analysis (%) calcd for $C_{25}H_{20}N_2O_2$: C, 78.95; H, 5.26; N, 7.37. Found: C, 78.90; H, 5.30; N, 7.38.

Preparation of L2. A solution of **L1** (0.76 g, 2.0 mmol) in anhydrous EtOH (80 mL) was heated to reflux for about 5 h. After cooling to room temperature, the solvent was removed under reduced pressure to give a yellow solid. The product was recrystallized from EtOH to give orange crystals of **L2**. Yield, 80%. IR (KBr pellet) ν (cm^{-1}) = 3100 (s), 2990 (s), 2850 (m), 2250 (vs), 1620 (m), 1595 (m), 1580 (s), 1530 (m), 1485 (vs), 1460 (s), 1385 (s), 1340 (vs), 1295 (s), 1225 (s), 1115 (s), 1020 (s), 960 (m), 920 (m), 845 (s), 805 (m), 780 (m), 745 (m), 700 (s). ^{1}H NMR (90 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.17−7.18 (m, 13H, $-C_6H_4$ and $-C_6H_5$), 6.94 (s, 2H, $-C_5H_2$), 1.33 (s, 9H, $-CH_3$). Elemental analysis (%) calcd for $C_{31}H_{24}N_4$: C, 83.30; H, 5.31; N, 12.39. Found: C, 83.14; H, 5.28; N, 12.25.

Preparation of L3. L3 was prepared following the procedure described for **L1** except by using 3-cyanobenzoyl chloride (2.00 g, 12.5 mmol) instead of 4-cyanobenzoyl chloride to afford orange crystalline solid (1.41 g, 59%). IR (KBr pellet) ν (cm^{-1}) = 3105 (s), 2995 (s), 2880 (s), 2250 (vs), 1630 (vs), 1605 (vs), 1550 (vs), 1515 (vs), 1415 (vs), 1365 (vs), 1350 (vs), 1170 (s), 1120 (s), 935 (s), 800 (m), 730 (s), 675 (m). ^{1}H NMR (90 MHz, $CDCl_3$, 25 °C, TMS): δ = 17.85 (s, 1H, −OH), 7.8 (m, 8H, $-C_6H_4$), 7.09 (s, 2H, $-C_5H_2$), 1.25 (s, 9H, $-CH_3$). Elemental analysis (%) calcd for $C_{25}H_{20}N_2O_2$: C, 78.95; H, 5.26; N, 7.37; O, 8.42. Found: C, 78.91; H, 5.28; N, 7.39.

Preparation of 1. A mixture of **L1** (7.6 mg, 0.02 mmol) and $Ag(ClO_4)\cdot H_2O$ (6.0 mg, 0.03 mmol) in benzene (20 mL) was stirred for 5 min. The clear orange solution was allowed to stand for a week at room temperature to afford orange crystals (6.3 mg, 54%, based on **L1**). IR (KBr pellet) γ (cm^{-1}) = 3145 (s), 2990 (s), 2850 (m), 2290 (m), 2255 (s), 1620 (s), 1600 (vs), 1520 (vs), 1415 (vs), 1370 (vs), 1350 (s), 1185 (m), 1110 (vs), 1090 (vs), 945 (s), 850 (m), 750 (w), 680 (w). Elemental analysis (%) calcd for $AgC_{46}H_{41}O_6N_2Cl$: C, 64.10; H, 4.76; N, 3.25. Found: C, 64.28; H, 5.00; N, 3.35. Crystals of **1** lose solvent molecules and turn opaque within several minutes under ambient atmosphere. Because of its instability, the host−guest chemistry of **1** could not be investigated.

Preparation of 2. A mixture of **L1** (19.1 mg, 0.05 mmol) and $Co(OAc)_2\cdot 2H_2O$ (5.3 mg, 0.025 mmol) in anhydrous EtOH (15 mL) was refluxed for 10 min and allowed to cool. The clear red-brown

Table 3. Interatomic Distances (Å) and Bond Angles (deg) with Estimated SDs () for **L2**−**L3** and **1**−**7**

L2			
C(1)−C(6)	1.372(2)	C(1)−C(2)	1.410(2)
C(1)−C(5)	1.460(2)	C(2)−C(3)	1.390(2)
C(3)−C(4)	1.424(2)	C(4)−C(5)	1.390(2)
C(14)−N(3)	1.328(2)	C(22)−N(2)	1.445(2)
N(2)−N(3)	1.361(2)	C(21)−N(4)	1.143(3)
C(6)−C(1)−C(2)	132.76(16)	C(6)−C(1)−C(5)	118.99(15)
C(2)−C(1)−C(5)	108.19(15)	N(2)−C(6)−C(1)	118.31(15)
C(6)−N(2)−N(3)	125.34(14)	N(3)−N(2)−C(22)	114.15(13)
L3			
C(1)−C(2)	1.408(2)	C(1)−C(5)	1.384(2)
C(4)−C(14)	1.395(2)	C(2)−C(3)	1.402(2)
C(3)−C(4)	1.468(2)	C(4)−C(5)	1.420(2)
C(6)−O(1)	1.273(2)	C(13)−N(1)	1.149(3)
C(5)−C(1)−C(2)	106.65(16)	C(5)−C(1)−C(22)	127.38(16)
C(3)−C(2)−C(1)	110.67(16)	C(2)−C(3)−C(6)	125.44(16)
O(1)−C(6)−C(7)	113.46(11)	O(1)−C(6)−C(7)	114.54(15)
1			
Ag−N(1)	2.139(2)	Ag−N(2)#1	2.169(2)
Ag−O(11)	2.5463(19)		
N(1)−Ag−N(2)#1	166.83(9)	N(1)−Ag−O(11)	114.11(8)
N(2)#1−Ag−O(11)	78.90(7)	C(2)−C(1)−C(5)	106.9(2)
2			
Co−O(1)#1	2.0022(16)	Co−O(1)	2.0022(16)
Co−O(2)	2.0052(16)	Co−O(3)	2.129(2)
O(1)#1−Co−O(1)	180.00(5)	O(1)#1−Co−O(2)	88.68(7)
O(2)−Co−O(2)#1	180.0	O(1)#1−Co−O(3)	84.71(9)
O(2)#1−Co−O(3)	89.18(9)	O(3)−Co−O(3)#1	180.0
3			
Ag(1)−N(4)#1	2.165(10)	Ag(1)−N(1)	2.166(10)
Ag(1)−C(2)#2	2.679(9)	Ag(2)−O(11)	2.290(13)
Ag(2)−N(2)	2.317(8)	Ag(2)−C(42)	2.444(16)
Ag(2)−C(41)	2.571(15)		
N(4)#1−Ag(1)−N(1)	160.5(4)	N(4)#1−Ag(1)−C(2)#2	101.8(3)
N(1)−Ag(1)−C(2)#2	94.0(3)	O(11)−Ag(2)−N(2)	112.7(5)
O(11)−Ag(2)−C(42)	113.0(6)	N(2)−Ag(2)−C(42)	133.5(4)
O(11)−Ag(2)−C(41)	137.0(6)	N(2)−Ag(2)−C(41)	108.8(5)
C(42)−Ag(2)−C(41)	31.2(5)	O(11)−Ag(2)−C(31)	93.0(5)
N(2)−Ag(2)−C(31)	70.0(2)	C(42)−Ag(2)−C(31)	115.5(5)
C(41)−Ag(2)−C(31)	90.7(4)	C(1)−C(2)−Ag(1)#2	84.4(5)
4			
Ag(1)−N(2)	2.199(4)	Ag(1)−N(4)#1	2.203(5)
Ag(1)−N(1)#2	2.327(4)		
N(2)−Ag(1)−N(4)#1	145.63(17)	N(2)−Ag(1)−N(1)#2	124.55(15)
N(4)#1−Ag(1)−N(1)#2	89.59(16)	N(2)−Ag(1)−C(22)	50.77(14)
N(4)#1−Ag(1)−C(22)	94.96(16)	N(1)#2−Ag(1)−C(22)	174.94(14)
N(2)−Ag(1)−N(3)	23.23(12)	N(4)#1−Ag(1)−N(3)	122.66(15)
N(1)#2−Ag(1)−N(3)	147.73(13)	C(22)−Ag(1)−N(3)	27.71(12)
5			
Ag(1)−N(1)	2.123(5)	Ag(1)−N(4)#1	2.147(5)
Ag(1)−F(11)	2.705(5)		
N(1)−Ag(1)−N(4)#1	172.4(2)	N(1)−Ag(1)−F(11)	85.39(19)
N(4)#1−Ag(1)−F(11)	88.2(2)	N(1)−Ag(1)−C(41)	90.0(2)
N(4)#1−Ag(1)−C(41)	95.6(2)	F(11)−Ag(1)−C(41)	169.1(2)
N(1)−Ag(1)−C(42)	97.3(2)	N(4)#1−Ag(1)−C(42)	85.7(2)
F(11)−Ag(1)−C(42)	144.8(2)	C(41)−Ag(1)−C(42)	26.3(2)
N(1)−Ag(1)−Cl(1)#2	88.53(16)	N(4)#1−Ag(1)−Cl(1)#2	85.08(16)
F(11)−Ag(1)−Cl(1)#2	64.77(13)	C(41)−Ag(1)−Cl(1)#2	105.33(16)
C(42)−Ag(1)−Cl(1)#2	80.22(17)		
6			
Ag−N(3)#1	2.294(4)	Ag−N(4)	2.301(4)
Ag−N(2)#2	2.316(4)	Ag−N(1)	2.338(4)
N(3)#1−Ag−N(4)	92.08(16)	N(3)#1−Ag−N(2)#2	107.37(15)
N(4)−Ag−N(2)#2	150.49(16)	N(3)#1−Ag−N(1)	121.29(16)
N(4)−Ag−N(1)	99.73(15)	N(2)#2−Ag−N(1)	89.08(15)
7			
Ag−N(1)	2.253(4)	Ag−N(2)#1	2.296(3)
Ag−N(3)	2.385(4)	Ag−N(4)#2	2.410(4)
N(1)−Ag−N(2)#1	143.38(15)	N(1)−Ag−N(3)	94.23(15)
N(2)#1−Ag−N(3)	105.39(14)	N(1)−Ag−N(4)#2	108.56(14)
N(2)#1−Ag−N(4)#2	82.48(14)	N(3)−Ag−N(4)#2	129.47(15)

solution was allowed to stand for a week at room temperature. Deep brown crystals were collected, washed with hexane, and dried in air (20.7 mg, 85%). IR (KBr pellet) γ (cm^{-1}) = 3500 (br), 2980 (m), 2850 (m), 2260 (s), 1610 (m), 1580 (s), 1550 (s), 1535 (s), 1417 (s), 1365 (w), 1330 (s), 1170 (s), 870 (m), 845 (m), 760 (w). Elemental analysis (%) calcd for $C_{54}H_{50}CoN_4O_6$: C, 71.22; H, 5.50; N, 6.15. Found: C, 71.23; H, 5.30; N, 6.09.

Preparation of 3. Compound **3** was synthesized by laying a benzene solution (7 mL) of $Ag(ClO_4)\cdot H_2O$ (11.0 mg, 0.055 mmol) over a methylene chloride solution of (5 mL) of **L2** (12.4 mg, 0.028 mmol) in 55% yield. IR (KBr pellet) γ (cm^{-1}) = 2980 (s), 2850 (m), 2280 (s), 2250 (m), 1610 (m), 1580 (s), 1490 (s), 1460 (s), 1390 (m), 1340 (s), 1290 (m), 1220 (m), 1100 (vs), 845 (s), 690 (s). Elemental analysis (%) calcd for $C_{43}H_{39}Ag_2Cl_2N_4O_{9.50}$: C, 49.12; H, 3.71; N, 5.33. Found: C, 49.14; H, 3.54; N, 5.28. Crystals of **3** lose solvent molecules and turn opaque within several minutes under ambient atmosphere. Because of its instability, the host−guest chemistry of **3** could not be investigated.

Preparation of 4 and 5. A solution of $AgSbF_6$ (12.0 mg, 0.035 mmol) in benzene was layered onto a solution of **L2** (15.8 mg, 0.035 mmol) in CH_2Cl_2 (5 mL). The solution was left for about one week at room temperature, and yellow crystals of **4** were obtained. Yield, 46%. IR (KBr, cm^{-1}): 2955 (s), 2850 (m), 2255 (s), 1580 (s), 1490 (s), 1394 (s), 1348 (s), 845 (s), 657 (vs). Anal. Calcd for $C_{31}H_{24}AgF_6N_4Sb\cdot 0.5C_6H_6$ (**4**): C, 48.85; H, 3.23; N, 6.71. Found: C, 49.19; H, 3.30; N, 6.71. Above solution was left to stand at room temperature for about two weeks, affording **5** as red crystals. Yield, 9%. IR (KBr, cm^{-1}): 2960 (s), 2850 (m), 2362 (m), 2333 (m),1628 (s), 1491 (s), 1397 (vs), 1022 (s), 847 (s), 660 (vs). Anal. Calcd for $C_{44}H_{38}AgCl_2F_{12}N_4Sb_2$ (**4**): C, 41.48; H, 2.98; N, 4.40. Found: C, 41.39; H, 3.05; N, 4.48.

Preparation of 6. A solution of **L3** (15.2 mg, 0.04 mmol) in benzene (15 mL) was mixed with a solution of $AgSbF_6$ (14.0 mg, 0.041 mmol) in CH_2Cl_2. The solutions were left for about three weeks at room temperature, and yellow crystals were obtained. Yield, 36%. IR (KBr, cm^{-1}): 3015 (m), 2970 (s), 2850 (m), 2300 (m), 2250 (vs), 1625 (vs), 1600 (vs), 1555 (vs), 1520 (vs), 1440 (vs), 1425 (vs), 1365 (vs), 1170 (m), 1120 (s), 930 (m), 800 (m), 750 (m), 725 (m), 665 (vs). Anal. Calcd for $C_{50}H_{40}AgF_6N_4O_4Sb$ (**6**): C, 54.32; H, 3.62; N, 5.07. Found: C, 54.35; H, 3.65; N, 5.03.

Preparation of 7. A solution of **L3** (15.2 mg, 0.04 mmol) in benzene (15 mL) was mixed with a solution of $AgSbF_6$ (14.0 mg, 0.041 mmol) in benzene. The solutions were left for about one week at room temperature, and yellow crystals were obtained. Yield, 60%. IR (KBr, cm^{-1}): 2970 (s), 2850 (m), 2300 (vs), 2250 (m), 1620 (vs), 1555 (vs), 1520 (vs), 1415 (vs), 1365 (vs), 1350 (s), 1174 (s), 1124 (s), 935 (m), 800 (m), 725 (m), 655 (vs). Anal. Calcd for $C_{50}H_{40}AgF_6N_4O_4Sb$ (**6**): C, 54.32; H, 3.62; N, 5.07. Found: C, 54.50; H, 3.46; N, 5.12.

Crystallography. Suitable single crystals of **L2**, **L3** and **1**−**7** were selected and mounted onto thin glass fibers. X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å). The raw frame data for **L2**, **L3** and **1**−**7** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[43] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[43] There was no evidence of crystal decay during data collection for any compound. The final unit cell parameters were determined by the least-squares refinement of all reflections from each data set with $I > 5\sigma(I)$ (5944 for **1**, 4588 for **2**, 5142 for **3**, 7259 for **4**, 7825 for **5**, 7562 for **6**, and 8511 for **7**). Space groups were determined by a combination of systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structures. All

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(43) SMART Version 5.624, SAINT Version 6.02, SADABS, and SHELX-TL Version 5.1. Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

structures were solved by direct methods followed by difference Fourier synthesis, and refined against F^2 by the full-matrix least squares technique, using SHELX.[43] **L2** crystallized in the space group $P2_1/n$. Two independent **L2** molecules are present in the asymmetric unit. The *tert*-butyl group of one is rotationally disordered over two positions in a 50:/50 ratio. An EtOH molecule of crystallization is also present, also disordered equally over two positions. **L3** crystallizes in the space group $P\bar{1}$. The asymmetric unit contains two crystallographically and conformationally inequivalent molecules. Compound **1** crystallizes in the space group $P\bar{1}$. The asymmetric unit consists of one Ag(I) center, one **L1** ligand, one ClO_4^- counterion, three full benzene molecules of crystallization, and another half-benzene located on an inversion center. Compound **2** also crystallizes in the space group $P\bar{1}$. The complex lies on a crystallographic inversion center. The *tert*-butyl substituent of the **L1** ligand is rotationally disordered over two orientations in the refined ratio 0.69(2):0.31(2). Compound **3** crystallizes in the space group $C2/c$. In general, precise refinement was hindered by the low quality of the available crystals and by extensive disorder, as reflected in the high *R*-factors. The present structural results should be regarded accordingly. Two Ag centers, one **L2** ligand, an η^2-coordinated C_6H_6 molecule, and a coordinated H_2O molecule were readily located in the asymmetric unit and refined anisotropically. The water hydrogen atoms could not be located and were not calculated. There are three independent ClO_4^- counterions in the asymmetric unit. Perchlorate Cl(1), near Ag(1), was located and refined anisotropically; however, the inflated displacement parameters for this species indicate unresolved disorder. Cl(2) was modeled as being disordered together in the same region with a C_6H_6 and a water molecule. The disorder model used was 50% occupancy ClO_4^-/H_2O and 50% C_6H_6. The C_6H_6 was refined as a rigid group, the ClO_4^- was restrained to adopt the same geometry as perchlorate Cl(1), and no H atoms were located or calculated for the water. All species of this disorder assembly were refined isotropically. Cl(3) is disordered about a 2-fold axis, and was refined surrounded by eight-half-occupied oxygen atoms. Occupancies and isotropic displacement parameters were fixed for the oxygen atoms. Half of another C_6H_6 molecule of crystallization on an inversion center completes the asymmetric unit. Compound **4** crystallizes in the space group $P4/n$. The asymmetric unit consists of the Ag center, one **L2** ligand, and an SbF_6^- anion disordered over two closely spaced positions. Occupancies of each SbF_6^- disorder component were adjusted manually until reasonable displacement parameters were achieved for each, whereupon they were fixed. The final occupancy values are 0.925/0.075. The geometry of the minor component was restrained to be similar to that of the major component, and all atoms of the minor component were refined isotropically. Additionally, the *tert*-butyl substituent of the ligand is rotationally disordered over two orientations in the refined ratio 0.80(2):0.20(2). The minor component of this group was refined isotropically. All other atoms except those noted were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and included as riding atoms. After location and refinement of the species described above, channels parallel to the *c*-axis containing many diffuse electron density peaks remained, at $(x,y) = (^1/_4,^1/_4)$. No satisfactory disorder model was attained for these peaks, assumed to be solvent species disordered about 4-fold axes, and therefore the program SQUEEZE was used.[44] SQUEEZE calculated a solvent-accessible region of 654.1 Å^3 (10.0% of the total unit cell volume), corresponding to 351 e$^-$/cell. The contribution of these regions of electron density was removed from the structure factor calculations. The final reported *F*(000), FW, and density reflect crystallographically identifiable species only. Compound **5** crystallizes in the space group $P2_1/c$. The *tert*-butyl substituent of the **L2** ligand is rotationally disordered over two orientations, and was refined with the aid of 10 C−C same-distance restraints. Occupancies for each disorder component were initially refined but subsequently fixed near the final refined values (0.65/0.35) for stability. Compound **6** crystallizes in the triclinic crystal system in the space group $P\bar{1}$. The asymmetric compound contains two independent ligands per Ag and SbF_6^- unit. The *tert*-butyl group of one ligand is disordered over two orientations in the refined ratio 0.66(1):0.34. Compound **7** crystallizes in the space group $C2/c$. All atoms are on positions of general crystallographic symmetry. Crystal data, data collection parameters, and refinement statistics for **L2**, **L3**, and **1**−**7** are listed in Tables 1 and 2. Relevant interatomic bond distances and bond angles for them are given in Table 3.

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Supporting Information Available: Crystallographic information files for the title compounds (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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