New Ag^I Organometallic Coordination Polymers and M^{II} ($M = Cu^{II}$ and Co^{II}) Inorganic Supramolecular Complexes Generated from New Fulvene-Type Ligands

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Keywords: Coordination polymers / Supramolecular chemistry / Silver / Cobalt / Copper

Two novel fulvene-type organic ligands **L1** and **L2** have been synthesized by aroylation reaction of substituted cyclopentadienyl anions. **L1** crystallized in the monoclinic space group $P2_1$, $a = 6.7498(4)$, $b = 20.5769(11)$, $c = 8.9532(5)$ Å, $\beta = 109.5060(10)°$, and $Z = 2$. **L2** crystallized in the triclinic space group $P\bar{1}$, $a = 11.4126(10)$, $b = 11.4763(10)$, $c = 11.7719(10)$ Å, $\alpha = 67.050(2)$, $\beta = 74.509(2)$, $\gamma = 61.148(2)°$, and $Z = 2$. The coordination chemistry of **L1** and **L2** has been investigated. One novel Ag^I-containing organometallic coordination polymer **3**, based on both Ag^I–C and Ag^I–N interactions, has been synthesized by combination of **L1** and $AgClO_4$ in a benzene/dichloromethane mixed-solvent system. Two new M^{II}-containing [M = Cu^{II} (**4**) and Co^{II} (**5**)] supramolecular complexes with seven-membered metalla-ring unit have been prepared by combination of **L2** and the corresponding $M(OAc)_2{\cdot}2H_2O$ (M = Cu^{II} and Co^{II}) salts in ethanol. The isostructural compounds **4** and **5** crystallized in the triclinic space group $P\bar{1}$ [**4**: $a = 8.8808(5)$, $b = 10.9928(7)$, $c = 14.2196(9)$ Å, $\alpha = 99.9750(10)$, $\beta = 95.8190(10)$, $\gamma = 93.5610(10)°$, and $Z = 1$; **5**: $a = 8.7964(10)$, $b = 10.8103(12)$, $c = 14.3765(15)$ Å, $\alpha = 99.681(2)$, $\beta = 95.930(2)$, $\gamma = 93.429(2)°$, and $Z = 1$]. In the solid state, molecular complexes **4** and **5** are bound by strong intermolecular N···O–H hydrogen bonds in a hand-in-hand fashion to give a novel one-dimensional chain motif.

Introduction

The construction of new inorganic−organic coordination polymers and supramolecular complexes through the rational combination of organic ligands and metal ions is of intense current interest.[1−3] Two types of organic ligands have proven popular in construction of coordination polymers or supramolecular complexes. The first type contains heteroatom donors separated by various spacers such as bipyridine-type or biphenyl-cyanide-type ligands,[4] and the second type contains sp^2 electron-rich carbon atoms, such as small aromatic molecules and polycyclic aromatic hydrocarbons.[5] During the past decade, a number of inorganic coordination polymers based on metal−heteroatom bonding interactions and organometallic coordination polymers based on metal−carbon bonding interactions have been generated successfully with various structural motifs. In contrast, coordination polymers or supramolecular complexes based on both metal−heteroatom and metal−carbon bonding interactions have received considerably less attention. In principle, such materials might exhibit enhanced physical properties, such as electrical conductivity or fluorescence resulting from the synergy between the two distinctly different types of interactions. We are investigating the coordination chemistry of fulvene-type ligands that could provide both heteroatom and carbon atoms as coordination sites (Scheme 1). Recently, a series of novel organometallic coordination polymers based on both metal−carbon and metal−heteroatom interactions were obtained in our laboratory.[6] Conversely, fulvene-type organic spacers act not only as multidentate ligands but also as chelating ligands. Their specific geometry affords a good opportunity to synthesize seven-membered metalla-ring complexes that are not achievable easily with other 1,4-diketone organic ligands.

We report here the synthesis and characterization of two new fulvene-type ligands (**L1** and **L2**), one new organometallic coordination polymer $[Ag(\mathbf{L1})(ClO_4)]{\cdot}CH_2Cl_2$ (**3**), based on both metal−heteroatom and metal−carbon interactions, and two new M^{II} ($M = Co^{II}$, Cu^{II}) seven-membered metalla-ring supramolecular complexes, $[Co(\mathbf{L2})_2(C_2H_5OH)_2]$ (**4**) and $[Cu(\mathbf{L2})_2(C_2H_5OH)_2]$ (**5**), based on them.

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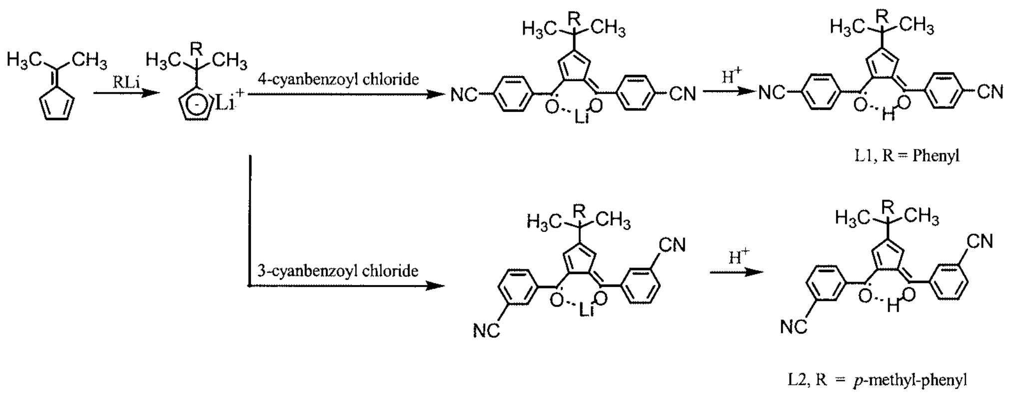
DOI: 10.1002/ejic.200300368



Scheme 1. Synthesis of ligands **L1** and **L2**

Results and Discussion

Synthesis and Structural Analysis of L1 and L2

Ligands **L1** and **L2** were prepared in moderate yields as deep-yellow crystalline solids by the respective reactions of 4- and 3-cyanobenzoyl chloride with substituted cyclopentadienyl anions, derived from 6,6′-dimethylfulvene and *p*-methylphenyllithium and phenyllithium in diethyl ether at 0 °C (Scheme 1). **L1** and **L2** are very soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, THF, and C_6H_6. Their structures were determined by ^1H NMR and IR spectroscopy, elemental analyses, and standard single-crystal X-ray diffraction techniques. Their IR spectra show −CN absorption bands at $\tilde{\nu} = 2250\ cm^{-1}$. In the ^1H NMR spectrum of **L1** and **L2** the proton resonances at $\delta = 18.20$ and 17.79 ppm as singlets, respectively, are due to the chelated proton, which is hydrogen-bonded to the neighboring carbonyl group on the 1-benzoyl group.[6,9] Their IR spectra do not show absorptions above 1630 cm^{-1} in the region normally assigned to organic carbonyl groups. However, the strong band at 1615 cm^{-1} is consistent with the hydrogen-bonded enol structure since conjugation and chelation lead to a large shift of the carbonyl infrared band. The structures of **L1** and **L2** were further confirmed by X-ray diffraction techniques. The corresponding molecular structures of **L1** and **L2** are shown in Figures 1 and 2, respectively; that of **L2** reveals that the two aroyl groups on the substituted cyclopentadienylenyl ring are adjacent. The C−C bonds on the substituted Cp ring and also C(3)−C(6) and C(4)−C(14) range from 1.377(2) to 1.468(2) Å, which are significantly shorter than a normal C−C single bond. Thus, **L2** is a fulvene[6,8] − an important organometallic moiety.[10] The enol hydrogen atom [H(1)] is hydrogen-bonded to the carbonyl oxygen atom [O(2), $d_{O(2)\cdots H(1)} = 1.35(3)$ Å, ∠O(1)−H(1)···O(2) = 171(2)° and $d_{O(1)\cdots O(2)} = 2.464(18)$ Å] to provide a hydrogen-bonded seven-membered ring. Interestingly, two $-C_6H_4-CN$-*m* rings and the hydrogen-bonded seven-membered ring are not in the same plane. The dihedral angles between the $-C_6H_4-CN$-*m* ring and the seven-membered ring are 10.4(3) and 13.4(3)°, respectively. In the solid state, two −*m*-CN functional groups on **L2** are oriented in opposite directions and the terminal (−CN) N···N separation is 17.32(5) Å. A similar molecular structure was found for **L1**, with a slightly shorter terminal (−CN) N···N separation [16.88(5) Å]. In addition to the two −CN groups, the carbonyl and enol groups in **L1** and **L2** could act as potential chelating coordinating sites to bind transition metal ions into seven-membered metalla-ring-containing complexes; they could also potentially be transferred to other types of organic functional groups, such as heterocycles, by reaction with hydroxylamine, hydrazine or the like.[6b] Compounds **L1** and **L2** are a new type of ligands that can be used to construct polymeric compounds containing both inorganic and organometallic moieties.

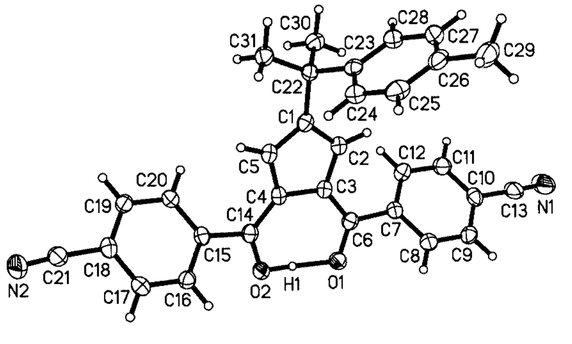


Figure 1. ORTEP plot of compound **L1** with 30% probability ellipsoids

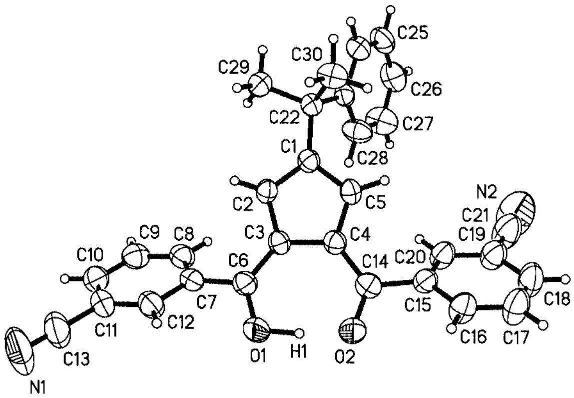


Figure 2. ORTEP plot of compound **L2** with 30% probability ellipsoids

Synthesis and Structural Analysis of 3

Silver-containing polymeric compound **3**, $[Ag(\mathbf{L1})(ClO_4)]\cdot CH_2Cl_2$, was synthesized in 85% yield by the combination of **L1** and $Ag(ClO_4)\cdot H_2O$ in a benzene/dichloromethane mixed-solvent system at ambient temperature. Crystals of **3** lose solvent molecules and turn opaque within several minutes under ambient atmosphere, preventing investigation of the host-guest chemistry of **3**. Single-crystal analysis revealed (Figure 3) a distorted tetrahedral coordination sphere around the silver atom, consisting of two N-donors [N(1) and N(2)] from two ligands **L1** [Ag−N(1) = 2.242(2) and Ag−N(1) = 2.242(2) 2.190(2) Å], one O-donor [O(11)] from the ClO_4^- counterion [Ag−O(11) = 2.416(2) Å], and one carbon atom [C(27)] from the *p*-methylphenyl group on the third ligand **L1**. The Ag−C distance is 2.763(3) Å while the remaining Ag−C contacts (> 2.958 Å) are beyond the limits (2.47−2.80 Å) commonly observed in Ag^I−aromatic complexes. Thus, the benzene ring in **L1** coordinates to the Ag^I ion with an η^1-bonding mode, which is normally observed in arene−metal complexes.[11]

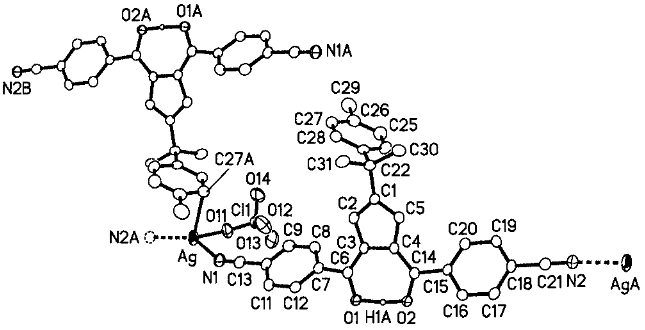


Figure 3. ORTEP plot of compound **3** with 30% probability ellipsoids

In the solid state, the silver centers are connected by **L1** through the two terminal −CN groups into mild zigzag one-dimensional chains which further associate into inversion-related pairs by Ag−C organometallic interactions along the crystallographic [211] direction (Figure 4). In addition, the ladder-like chains stack together to create two kinds of rectangular channels: large ones along the crystallographic [100] direction (crystallographic dimensions of the rings ca. 14 × 12 Å), which are filled by CH_2Cl_2 guest molecules (Figure 5, a), and small ones (around 10 × 10 Å) that extend along the crystallographic [011] direction, in which both ClO_4^- counterions and CH_2Cl_2 guest molecules are located (Figure 5, b). Extended frameworks composed of organic spacers containing heteroatom donors via metal−heteroatom coordination bonds[4] and organometallic coordination polymers generated from smaller aromatics and also polycyclic aromatic hydrocarbons based on cation−π interactions[5] are well established; however, supramolecular complexes based on both metal−aromatic carbon and metal−heteroatom interactions appear to be quite unusual. A related example is the coordination of the rigid tridentate ligand 1-(4-cyanobenzoyl)-6-(4-cyanophenyl)-6-hydroxy-3-(4-phenylcyclohexyl)fulvene with AgOTf in benzene that led to the open-framework material $[Ag_2(C_{33}H_{26}N_2O_2)(H_2O)_2(SO_3CF_3)_2]\cdot 0.5C_6H_6$,[6a] which contains 21 × 15 Å parallelogram-like channels in which benzene guest molecules are located.[6a] The smaller chan-

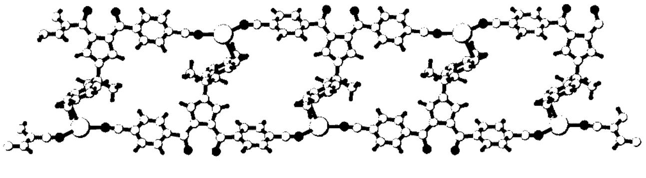


Figure 4. One-dimensional organometallic chain found in **3** (along crystallographic [211] direction), H atoms, ClO_4^- counterions and CH_2Cl_2 guest molecules are omitted for clarity

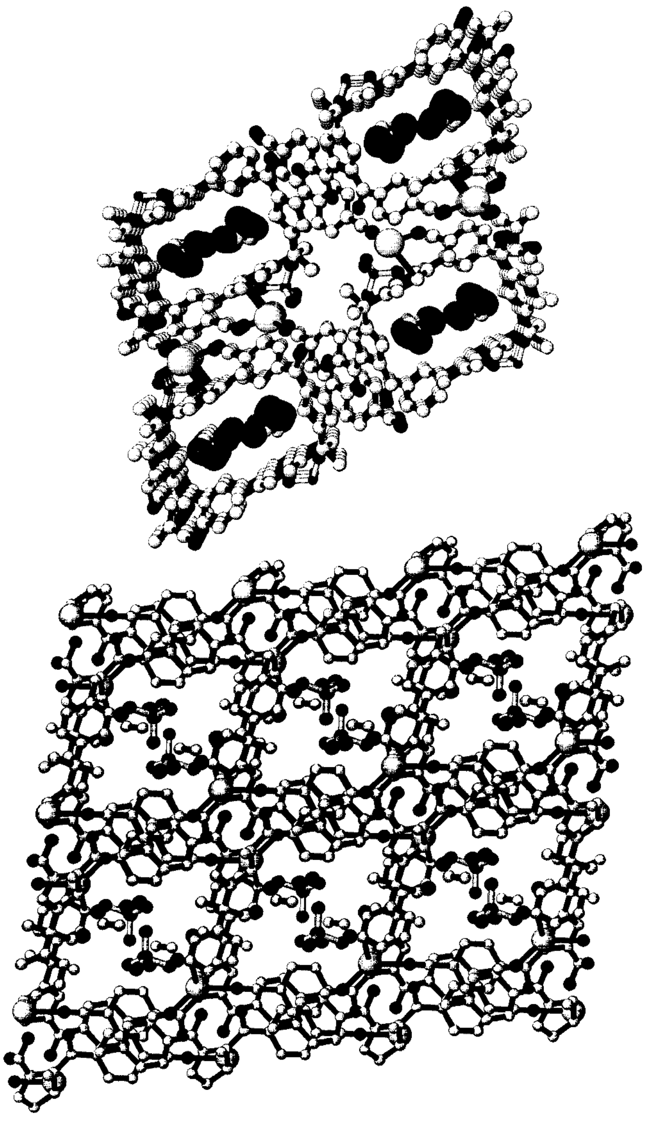


Figure 5. Top: channels in **3** (down the *a* axis), H atoms are omitted for clarity; bottom: channels in **3** (down the [011] direction), H atoms are omitted for clarity

nels found in **3**, however, differ in shape (rectangle-like in **3**, Figure 5) due to the different coordination mode of the silver(I) ion and the different templating effect of counterions.

To confirm **L1** as a chelating ligand to bind metal ions by two carbonyl oxygen atoms, $M(OAc)_2 \cdot 2H_2O$ (M = Cu^{II}, Co^{II}) were used instead of inorganic Ag^I salts in the reactions in ethanol. Elemental analyses and IR spectra showed that the resultant compounds have the chemical formula $[M(\mathbf{L1})_2(C_2H_5OH)_2]$. Unfortunately, no single-crystal structures were obtained. To confirm the structures by single-crystal X-ray diffraction, ligand **L2** was treated instead of **L1** under the same conditions.

Synthesis and Structural Analysis of 4 and 5

Synthesis

Complexes **4** and **5** were synthesized by solution reactions between the new **L2** and $Cu(OAc)_2 \cdot 2H_2O$ and $Co(OAc)_2 \cdot 2H_2O$ in ethanol, respectively. When a solution of **L2** in ethanol was treated with $Cu(OAc)_2 \cdot 2H_2O$ and $Co(OAc)_2 \cdot 2H_2O$, respectively, in a metal/ligand molar ratio of 1:2, compounds **4** and **5** were obtained as neutral molecular compounds with seven-membered metalla-rings. It is noteworthy that the coordination chemistry of **L2** with transition metal templates Cu^{II} and Co^{II} is independent of the metal/ligand molar ratio. For example, ratios of 2:1 and even 3:1 yielded **4** and **5** as the only products.

Structural Analysis of Compounds 4 and 5

Compounds **4** and **5** are isostructural and crystallize in the triclinic system. For example, the Cu^{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 (Figure 6). The octahedral coordination polyhedron is slightly distorted — all angles around the copper center deviate significantly from 90° [O(1)−Cu−O(2) = 93.85(7)°, O(1)−Cu−O(3) = 87.77(8)°, O(2)−Cu−O(3) = 96.99(8)°]. The Cu−O bond lengths on the basal plane are 1.9318(15) and 1.9451(16) Å, respectively, which compare well with the Cu−O distance found in copper−oxygen complexes (e.g., $[Cu(C_6O_4Cl_2)(C_4H_4N_2)]$,[12] $[Cu(HLOX)Ni(N_3)]_2 \cdot 2CH_3OH$[13]). The distances between the copper center and the two axial O-donor atoms are the same [d_{Cu-O} = 2.390(2) Å], again consistent with the corresponding bond lengths in, for example, $Ag[Cu(2\text{-pyrazinecarboxylate})_2](H_2O)(NO_3)$[14] and $[Cu(HBIP)(C_2O_4)(H_2O)] \cdot 2H_2O$.[15] 1,2-Diketone or 1,3-diketone compounds are known to chelate transition metal ions into five- or six-membered metalla-ring systems which engender less strain (Scheme 2),[16] because the atoms on the rings are allowed to adopt more closely their natural bond angles. However, seven-membered metalla-ring complexes generated from 1,4-diketone-containing ligands and transition metal ions are much less known, probably due to conformational strain.[16] **L2** reported herein, however, is perfect for the synthesis of such complexes because of its specific molecular geometry. In **4**, the carbon−carbon bond lengths on the substituted Cp ring and also the exocyclic carbon−carbon double bonds are almost the same as their corresponding bond lengths in the free ligand **L2** [ranging from 1.393(2) to 1.457(2) Å]. The four −CN groups in **4** are uncoordinated as two pairs oriented in opposite directions. The IR spectrum of **4** shows that the −C≡N stretch (2260 cm^{-1}) in **4** is essentially unchanged from that of the free ligand **L2**, indicating that the nitrile nitrogen atom does not enter the coordination sphere of the Cu^{II} center. A similar phenomenon occurs in the reaction of $[Ru_2\{O_2C(CH_2)_6CH_3\}_4]$ in toluene and $[Cu(hfacac)_2] \cdot H_2O$ (hfacac = hexafluoroacetylacetonate) in dichloromethane with 4-cyanopyridine and 3-cyanopyridine, respectively.[17] The discrete molecular 1:2 adducts $[Ru_2\{O_2C(CH_2)_6CH_3\}_4(4\text{-cyanopyridine})_2]$ and $[Cu(hfacac)_2(3\text{-cyanopyridine})_2]$ were obtained instead of the expected 4-cyanopyridine- and 3-cyanopyridine-bridged transition metal complexes. 4-Cyanopyridine and 3-cyanopyridine spacers have been used as bridging ligands to link transition metal species into dimers and polymers.[18,19] It appears that the nitrile N-donor atom has a poor coordinating ability to effectively link 3d metal ions. For example, in $[Cu(4\text{-cyanopyridine})_4(H_2O)(ClO_4)_2]_n$ the nitrile nitrogen atom only weakly coordinates with copper centers through a "semi-coordinated" bond [Cu−N≡C 2.649(4) Å], which is much longer than a normal Cu−N coordinative bond.[20] It is noteworthy that **4** contains uncoordinated N-donors, which have recently been suggested as potential new metal-containing building blocks,[21] that 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 **L2** (a possibility that we are pursuing).

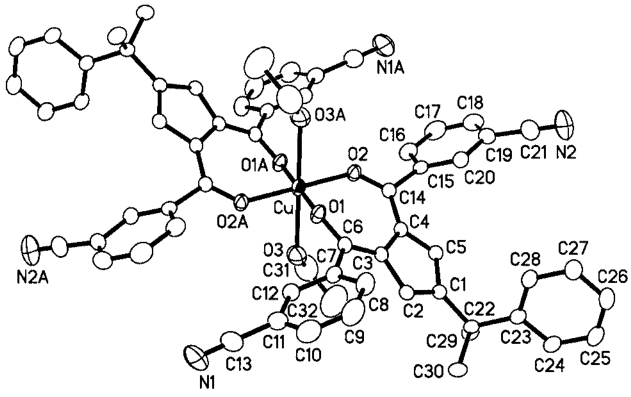
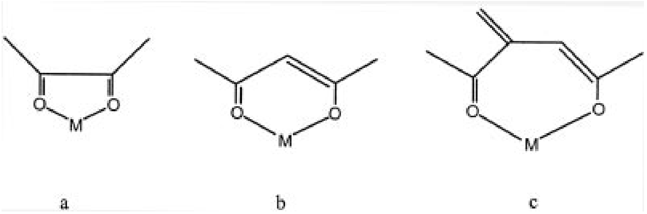


Figure 6. ORTEP plot of compound **4** with 30% probability ellipsoids

In the solid state (Figure 7) the neutral building blocks **4** arrange parallel to the crystallographic *c* axis, and moreover are bound by strong intermolecular N···O−H hydrogen bonds in a hand-in-hand fashion to create a one-dimensional chain motif along the crystallographic *b* axis. The hydrogen-bonding system in **4** consists of the one uncoordi-



Scheme 2. Five-membered metalla-ring (a); six-membered metalla-ring (b); seven-membered-ring (c)

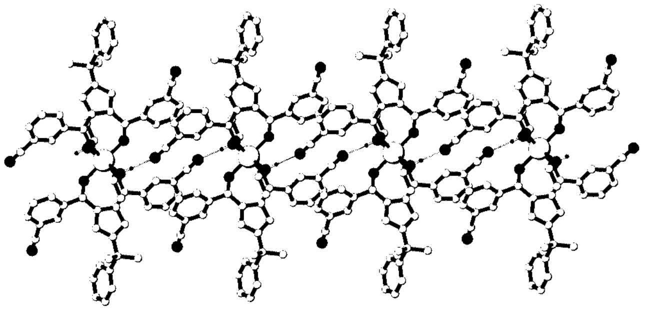


Figure 7. Hydrogen-bonded one-dimensional chain motif found in compounds **4** and **5**; hydrogen bonds are shown as dotted lines; this view is down the *a* axis

nated nitrogen atom N(1) on a −CN group with the hydrogen atom H(3) on the coordinated ethanol molecule O(3) of a neighboring Cu^{II} complex. The N(1)···H(3) distance is 1.94(2) Å. The corresponding O(3)···N(1) distance is 2.906(4) Å, and the corresponding O(3)−H(3)···N(1) angle is 170(4)°. The existence and structural importance of strong hydrogen-bonding interactions generated from −CN (as the hydrogen-bond acceptor) are now well established and have been observed in many compounds.[22] These strong hydrogen-bonding interactions contribute significantly to the alignment of the molecules of **4** in the crystalline state. The intrachain Cu···Cu distance is 10.99(3) Å.

In compound **5**, the Co^{II} center adopts a distorted octahedral $\{CoO_6\}$ coordination sphere, which is identical with the $\{CuO_6\}$ coordination environment found in **4**. In the corresponding single-crystal structure of **5** (Figure 8) the Co−O bond lengths on the basal plane lie in the range of 2.0059(19)−2.0226(16) Å. The distance between the Co^{II} center atom and the axial O-donor atom is 2.1385(19) Å, which is significantly longer than the equatorial Co−O distance. However, it is similar to the bond lengths in other Co^{II} compounds.[23]

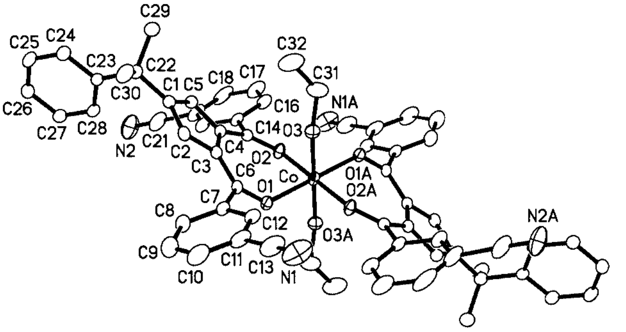


Figure 8. ORTEP plot of compound **5** with 30% probability ellipsoids

In the solid state, compound **5** presents the same hydrogen-bonded one-dimensional chain as in **4** (Figure 7). The N···H distance is 1.94(2) Å and the corresponding O···N distance is 2.906(4) Å, with a corresponding O−H···N angle of 170(4)°.

Luminescent Properties

The fluorescence properties and potential applications as light-emitting diodes (LEDs) of aromatic organic molecules, all-organic polymers and mixed inorganic−organic hybrid coordination polymers have been investigated.[24] Owing to the higher thermal stability of inorganic−organic coordination polymers and the ability to alter 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 electroluminescent materials.[25] The luminescent properties of the free ligand **L2**, and its metal complexes **4** and **5** have been investigated in the solid state and CH_2Cl_2 solution. In the solid-state spectra of **L2**, **4**, and **5** (Figure 9) **L2** exhibits one emission maximum at 523 nm and complexes **4** and **5** exhibit emission bands that are blue-shifted to 346 nm and 347 nm, respectively; however, the fluorescence intensity was not enhanced. The emission maximum of **L2** in CH_2Cl_2 is at 542 nm, and those of complexes **4** and **5** in CH_2Cl_2 are blue-shift to 518 nm and 521 nm, respectively (Figure 10). Due to its instability, the luminescent properties of **3** could not be investigated. In summary, the emission color of free **L2** is significantly affected by its incorporation into the M-containing (M = Co^{II} and Cu^{II}) complexes.

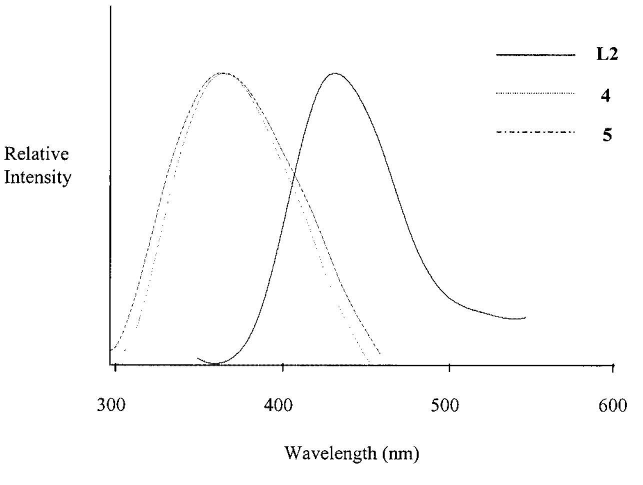


Figure 9. Photo-induced emission spectra of **L2**, **4**, and **5** in the solid state at room temperature

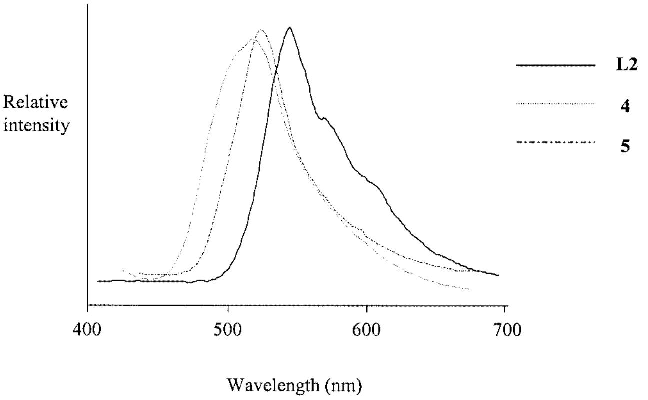


Figure 10. Photo-induced emission spectra of **L2**, **4**, and **5** in CH_2Cl_2 at room temperature

Conclusions

The two new fulvene-type ligands **L1** and **L2**, synthesized by the aroylation of substituted cyclopentadienyl anions, have been shown to be tridentate or bidentate chelating ligands to coordinate transition metal ions into coordination polymers or supramolecular complexes. The specific coordination behavior of ligand **1** resulted in a novel a Ag^I-containing organometallic coordination polymer (**3**) based on both metal−carbon and metal−heteroatom interactions. The special geometry of **2** resulted in complexes **4** and **5** with unusual seven-membered metalla-ring structures. In the solid state, **4** and **5** adopt a novel hydrogen-bonded one-dimensional chain motif. We are currently preparing new such fulvene ligands, with different substituted organic functional groups, so as to construct various new transition metal complexes and coordination polymers (including dimetallic polymeric compounds) with potentially novel structures.

Experimental Section

Materials and Methods: 4-Cyanobenzoyl chloride, 3-cyanobenzoyl chloride, 6,6′-dimethylfulvene, and aryllithium were prepared according to literature methods.[7] 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. ^1H NMR spectroscopic data were collected using a JEOL FX 90Q NMR spectrometer. Chemical shifts (δ) are relative to TMS. Element analyses were performed with a Perkin−Elmer Model 240C analyzer.

Preparation of L1: A solution of 4-cyanobenzoyl chloride (1.80 g, 10.8 mmol) in anhydrous diethyl ether (20 mL) was added dropwise to a solution of substituted cyclopentadienyl anions (16.2 mmol) in anhydrous diethyl ether at 0 °C, which in turn was derived from 6,6′-dimethylfulvene (16.2 mmol) and 4-methylphenyllithium (16.2 mmol) in anhydrous diethyl ether. The mixture was then stirred at room temperature overnight. The solvent was then reduced to about 10 mL under vacuum. Hexane was added and an orange solid precipitated that 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, 6:5) to afford an orange crystalline solid in 50% yield. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3110 (w), 2250 (s), 1635 (s), 1600 (s), 1575 (m), 1540 (vs), 1500 (m), 1475 (s), 1413 (vs), 1410 (s), 1365 (s), 845 (m). ^1H NMR (90 MHz, $CDCl_3$, 25 °C, TMS, ppm): δ = 18.20 (s, 1 H, OH), 7.85 (s, 8 H, C_6H_4), 7.25, 7.20 (d, 2 H, C_5H_3), 6.57 (t, 1 H, C_5H_3). $C_{21}H_{13}N_2O_2$ (456.52): calcd. C 77.78, H 4.01, N 8.64; found C 77.80, H 4.00, N 8.66.

Preparation of L2: A solution of 3-cyanobenzoyl chloride (1.47 g, 8.87 mmol) in anhydrous diethyl ether (20 mL) was added dropwise into a solution of substituted cyclopentadienyl anions (13.3 mmol) in anhydrous diethyl ether (20 mL) at 0 °C, which derived from 6,6′-dimethylfulvene (13.3 mmol) and phenyllithium (13.3 mmol) in anhydrous diethyl ether. The mixture was then stirred at room temperature overnight, and the solvent then reduced to about 10 mL under vacuum. Hexane was subsequently added and an orange solid precipitated, which was then 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, 3:2) to afford an orange crystalline solid (1.0 g, 51%). IR (KBr pellet, cm^{-1}) $\tilde{\nu}$ = 2995 (m), 2885 (w), 2250 (s), 1615 (s), 1590 (s), 1555 (m), 1525 (s), 1490 (m), 1435 (s), 1415 (s), 1347 (s), 760 (s). ^1H NMR (90 MHz, $CDCl_3$, 25 °C, TMS, ppm): δ = 17.74 (s, 1 H, -OH), 7.99−7.51 (m, 8 H, C_6H_4), 7.25 (s, 5 H, C_6H_5), 6.96 (s, 2 H, C_5H_2), 1.61 (s, 6 H, CH_3). $C_{30}H_{22}N_2O_2{\cdot}0.5CH_3OH$ (458.52): calcd. C 79.82, H 5.23, N 6.11; found C 79.80, H 5.22, N 6.10.

Preparation of 3: Compound **3** was synthesized in 85% yield by layering a benzene solution (4 mL) of $Ag(ClO_4){\cdot}H_2O$ (9.5 mg, 0.046 mmol) over a dichloromethane solution (4 mL) of **L1** (13.9 mg, 0.03 mmol). IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 2998 (s), 2920 (w), 2280 (s), 2250 (m), 1615 (w), 1595 (s), 1540 (w), 1510 (s), 1435 (m), 1410 (m), 1350(s), 1255 (vs), 1180 (s), 1100 (vs), 850 (s). $C_{32}H_{26}AgCl_3N_2O_6$ (748.77): calcd. C 51.28, H 3.47, N 3.74; found C 51.49, H 3.54, N 3.75. Crystals of **3** lose solvent molecules and turn opaque within several minutes under ambient atmosphere, and so the host-guest chemistry of **3** could not be investigated.

Preparation of 4: A mixture of **L2** (24 mg, 0.054 mmol) and $Cu(OAc)_2{\cdot}2H_2O$ (5 mg, 0.027 mmol) in anhydrous EtOH (15 mL) was heated under reflux for 5 min and allowed to cool. The resultant clear red-brown solution was allowed to stand for a week at room temperature. Deep brown crystals were then collected, washed with hexane and dried in air (80% yield). IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3510 (br), 2990 (m), 2260 (s), 1600 (m), 1584 (s), 1555 (vs), 1530 (s), 1490 (w), 1450 (w), 1415 (s), 1360 (m), 1335 (s), 1310 (s), 775 (s). $C_{64}H_{54}CuN_4O_6$ (1038.65): calcd. C 73.94, H 5.20, N 5.39; found C 74.01, H 5.30, N 5.36.

Preparation of 5: A mixture of **L2** (24 mg, 0.054 mmol) and $Co(OAc)_2{\cdot}2H_2O$ (7 mg, 0.027 mmol) in anhydrous EtOH (15 mL) was heated under reflux for 5 min and allowed to cool. The clear red solution was allowed to stand at room temperature for 3 d. Deep red crystals were collected, washed with hexane and dried in air (95% yield). IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3475 (br), 2995 (m), 2260 (s), 1600 (m), 1585 (s), 1560 (vs), 1530 (s), 1494 (s), 1440 (w), 1430 (m), 1415 (s), 1360 (m), 1315 (s), 775 (s). $C_{64}H_{54}CoN_4O_6$ (1034.04): calcd. C 74.27, H 5.22, N 5.42; found C 74.27, H 5.23, N 5.38.

Crystal Structure Determination: Suitable single crystals of **L1**, **L2** and **3−5** were selected and epoxied in inert oil onto thin glass fibers. X-ray intensity data were measured with a Bruker SMART

Table 1. Crystallographic data for **L1**, **L2**, and **3**

	L1	**L2**	**3**
Empirical formula	$C_{31}H_{24}N_2O_2$	$C_{30}H_{22}N_2O_2{\cdot}0.5CH_3OH$	$C_{32}H_{26}AgCl_3N_2O_6$
Formula mass	456.52	458.52	748.77
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$
a [Å]	6.7498(4)	11.4126(10)	10.0147(8)
b [Å]	20.5769(11)	11.4763(10)	12.6221(10)
c [Å]	8.9532(5)	11.7719(10)	14.1054(11)
α [°]	90	67.050(2)	108.9110(10)
β [°]	109.5060(10)	74.509(2)	92.025(2)
γ [°]	90	61.148(2)	112.2560(10)
V [Å^3]	1172.14(11)	1237.57(19)	1535.5(2)
Z	2	2	2
ρ(calcd.) [g/cm^3]	1.293	1.230	1.620
μ(Mo-K_α) [mm^{-1}]	0.079	0.079	0.378
Temperature [K]	150	293	150
No. of refl. ($I > 3\sigma$)	5247	5084	6280
Residuals:			
$R1$; $wR2$ (all data)	0.0434; 0.0868	0.0919; 0.1066	0.0428; 0.0866

APEX CCD-based diffractometer system (Mo-K_α radiation, λ = 0.71073 Å). Recollection of the first 50 frames at the end of the process revealed no significant crystal decay. The raw frame data for all new compounds were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[8] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[8] All structures were solved by direct methods and refined against F^2 by the full-matrix least-squares technique. Hydrogen atoms were calculated and refined as riding atoms; all non-hydrogen atoms were refined with anisotropic displacement parameters. For compounds **4** and **5**, one C_6H_4CN group of the $C_{30}H_{21}N_2O_2$ ligand was found to be rotationally disordered over two orientations in ratios of 0.675:0.325 (**4**) and 0.78:0.22 (**5**). Solution and refinement in the space group $P1$ did not remove the disorder; the space group $P\bar{1}$ was therefore retained. Crystal data, data collection parameters, and refinement statistics for **L1** and **L2** and **3**−**5** are listed in Tables 1 and 2. Selected interatomic bond lengths and bond angles for **L1** and **L2** and **3**−**5** are given in Tables 3, 4, 5, 6, and 7. CCDC-175505 (**L1**), -191568 (**L2**), -175506 (**3**), -191569 (**4**), and -191570 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.

Table 2. Crystallographic data for **4** and **5**

	4	**5**
Empirical formula	$CuC_{64}H_{54}N_4O_6$	$CoC_{64}H_{54}N_4O_6$
Formula mass	1038.65	1034.04
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	8.8803(5)	8.7946(10)
b [Å]	10.9928(7)	10.8103(12)
c [Å]	14.2156(9)	14.3765(15)
α [°]	99.9750(10)	99.681(2)
β [°]	95.8190(10)	95.930(2)
γ [°]	93.5610(10)	93.429(2)
V [Å^3]	1355.19(14)	1336.0(3)
Z	1	1
ρ(calcd.) [g/cm^3]	1.273	1.285
μ(Mo-K_α) [mm^{-1}]	0.459	0.378
Temperature [°C]	293	190
No. of refl. ($I > 3\sigma$)	5525	4706
Residuals:		
$R1$; $wR2$ (all data)	0.0655; 0.1330	0.0728; 0.0939

Table 3. Interatomic distances [Å] and bond angles [°] with estimated standard deviations (in parantheses) for **1**

C(1)−C(2)	1.414(2)	C(1)−C(5)	1.378(2)
C(1)−C(22)	1.516(2)	C(2)−C(3)	1.386(2)
C(3)−C(6)	1.419(2)	C(3)−C(4)	1.476(2)
C(6)−O(1)	1.270(2)	C(6)−C(7)	1.488(2)
C(7)−C(8)	1.396(2)	C(13)−N(1)	1.136(2)
C(2)−C(1)−C(5)	107.02(14)	C(2)−C(1)−C(22)	124.76(14)
C(1)−C(2)−C(3)	110.87(13)	C(6)−C(3)−C(2)	125.69(14)
O(1)−C(6)−C(7)	114.23(14)	C(9)−C(10)−C(11)	120.77(15)
C(10)−C(11)−C(12)	119.90(15)	N(1)−C(13)−C(10)	177.6(2)

Table 4. Interatomic distances [Å] and bond angles [°] with estimated standard deviations (in parantheses) for **2**

C(1)−C(2)	1.337(2)	C(1)−C(5)	1.415(2)
C(1)−C(22)	1.513(2)	C(2)−C(3)	1.427(2)
C(3)−C(6)	1.386(2)	C(3)−C(4)	1.468(2)
C(6)−O(1)	1.307(2)	C(6)−C(7)	1.483(2)
C(7)−C(8)	1.380(3)	C(13)−N(1)	1.134(3)
C(2)−C(1)−C(5)	106.94(16)	C(2)−C(1)−C(22)	128.09(16)
C(1)−C(2)−C(3)	110.42(16)	C(6)−C(3)−C(2)	125.46(17)
O(1)−C(6)−C(7)	112.90(16)	C(9)−C(10)−C(11)	119.5(2)
C(10)−C(11)−C(13)	118.9(2)	N(1)−C(13)−C(11)	178.2(3)

Table 5. Interatomic distances [Å] and bond angles [°] with estimated standard deviations (in parentheses) for **3** (symmetry transformations used to generate equivalent atoms: #1: $x - 2$, $y - 1$, $z - 1$; #2: $-x + 1$, $-y + 1$, $-z + 1$; #3: $-x + 1$, $-y$, $-z + 1$; #4: $x + 2$, $y + 1$, $z + 1$)

Ag−N(2)#1	2.190(2)	Ag−N(1)	2.242(2)
Ag−O(11)	2.390(2)	Ag−O(11)	2.416(2)
Ag−C(27)#2	2.763(3)		
N(2)#1−Ag−N(1)	136.21(8)	N(2)#1−Ag−O(11)	117.55(7)
N(1)−Ag−O(11)	100.86(8)	N(2)#1−Ag−C(27)#2	108.55(8)
N(1)−Ag−C(27)#2	82.23(8)	O(11)−Ag−C(27)#2	100.75(7)

html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 6. Interatomic distances [Å] and bond angles [°] with estimated standard deviations (in parantehses) for **4** (symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $-z+1$)

Cu(1)−O(1)	1.9318(15)	Cu−O(2)	1.9451(16)
Cu−O(3)	2.390(2)		
O(1)#1−Cu−O(1)	180.00(7)	O(1)#1−Cu−O(2)#1	93.58(7)
O(2)#1−Cu−O(3)	83.01(7)	O(2)−Cu−O(3)	96.99(8)
O(1)−Cu−O(3)	87.77(8)	O(3)−C(31)−C(32)	112.2(8)
C(6)−O(1)−Cu	131.58(15)	C(14)−O(2)−Cu	135.22(15)
C(31)−O(3)−Cu	131.7 (5)	O(2)−C(14)−C(15)	113.7(2)

Table 7. Interatomic distances [Å] and bond angles [°] with estimated standard deviations (in parantehses) for **5** (symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $-z+1$)

Co(1)−O(1)	2.0059(19)	Co−O(2)	2.0226(16)
Co−O(3)	2.1385(19)		
O(1)#1−Co−O(1)	180.00(7)	O(1)#1−Co−O(2)#1	90.98(7)
O(2)#1−Co−O(3)	85.82(7)	O(2)−Co−O(3)	94.18(7)
O(1)−Co−O(3)	88.28(8)	O(3)−C(31)−C(32)	114.0(3)
C(6)−O(1)−Co	130.50(18)	C(14)−O(2)−Co	137.03(18)
C(31)−O(3)−Co	126.83(18)	O(2)−C(14)−C(15)	113.9(2)

Acknowledgments

We are grateful for financial support from the National Natural Science Foundation of China (No. 20174023), Shangdong Natural Science Foundation (No. Z2001B01) and Young Scientists Funding of Shandong Province of P. R. China; we also acknowledge financial support from the Starting Funding of China for overseas scholar.

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[1] [1a] T. Iwamoto, in: *Inclusion Compounds: Inorganic and physical Aspects of Inclusion* (Eds.: T. Iwamoto, J. L. Atwood, J. E. D. Davies, D. D. MacNicol), Oxford University Press, Oxford, **1991**, vol. 5, chapter 6, pp. 177. [1b] R. Robson, B. F. Abrahms, S. R. Batten, R. W. Gable, B. F. Hoskin, F. Liu, in: *Supramolecular Architecture* (Ed.: T. Bein), American Chemical Society, Washington, DC, **1992**, pp. 256. [1c]K. A. Hirsch, S. R. Wilson, J. S. Moore, *Inorg. Chem.* **1997**, *36*, 2960−2974.

[2] [2a] O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **1995**, *117*, 10401−10402. [2b] O. M. Yaghi, H. Li, T. L. Groy, *J. Am. Chem. Soc.* **1996**, *118*, 9096−9101.

[3] [3a] M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 7287−7288. [3b] K. N. Power, T. L. Hennigar, M. J. Zaworotko, *Chem. Commun.* **1998**, 595−596.

[4] [4a] P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798−2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638−2684, and references cited therein. [4b] A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117−138, and references cited therein.

[5] [5a] G. L. Ning, L. P. Wu, K. Sugimoto, M. Munakata, T. Kuroda-Sowa, M. Mackawa, *J. Chem. Soc., Dalton Trans.* **1999**, 2529−2536, and references cited therein. [5b] M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, G. L. Ning, T. Kojima, *J. Am. Chem. Soc.* **1998**, *120*, 8610−8618.

[6] [6a] Y.-B. Dong, G.-X. Jin, M. D. Smith, R-Q. Huang, B. Tang, H.-C. zur Loye, *Inorg. Chem.* **2002**, *41*, 4909−4914. [6b] Y.-B. Dong et al., unpublished results.

[7] [7a] A. Dormond, *J. Organomet. Chem.* **1975**, *101*, 71−78. [7b] R. A. Howie, *J. Organomet. Chem.* **1986**, *303*, 213−216.

[8] Bruker Analytical X-ray Systems, Inc., Madison, WI, **1999**.

[9] J. L. William, H. S. William, *J. Am. Chem. Soc.* **1957**, *79*, 4970−4973.

[10] K. J. Stone, R. D. Little, *J. Org. Chem.* **1984**, *49*, 1849−1852.

[11] M. Munakata, L. P. Wu, G. L. Ning, *Coord. Chem. Rev.* **2000**, *198*, 171−203.

[12] S. Kawata, S. Kitagawa, M. Kondo, I. Furuchi, M. Munakata, *Angew. Chem. Int. Ed. Engel.* **1994**, *33*, 1759−1761.

[13] C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **2000**, 251−258.

[14] Y.-B. Dong, M. D. Smith, H.-C. zur Loye, *Solid State Sci.* **2000**, *2*, 335−341.

[15] Y. Akhriff, J. Server, A. Sancho, J. Garcia, E. Escriva, J. V. Folgado, L. Soto, *Inorg. Chem.* **1999**, *38*, 1174−1185.

[16] P. Guerriero, S. Tamburini, P. A. Vigato, *Coord. Chem. Rev.* **1995**, *139*, 17−243.

[17] J. L. Wesemann, M. H. Chisholm, *Inorg. Chem.* **1997**, *36*, 3258−3267.

[18] [18a] H. Y. Hung, W. J. Chen, G. C. Yang, A. Yeh, *Inorg. Chem.* **1991**, *30*, 1862−1868. [18b] A. Benaltabef, S. B. R. Degllo, M. E. Folquer, N. E. Katz, *Inorg. Chim. Acta* **1991**, *188*, 67−70. [18c] A. E. Almaraz, L. A. Gentil, L. M. Baraldo, J. A. Olabe, *Inorg. Chem.* **1996**, *35*, 7718−7727.

[19] [19a] R. D. Bailey, L. L. Hook, W. T. Pennington, *Chem. Commun.* **1998**, 1181−1182. [19b] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *J. Chem. Soc., Chem. Commun.* **1994**, 2755−2756.

[20] W. R. Zhang, J. R. Jeitler, M. M. Turnbull, C. P. Landee, M. Y. Wei, R. D. Willet, *Inorg. Chim. Acta* **1997**, *256*, 183−198.

[21] H.-P. Wu, C. Janiak, G. Rheinwald, H. Lang, *J. Chem. Soc., Dalton Trans.* **1999**, 183−190.

[22] G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375−1405.

[23] Y.-B. Dong, M. D. Smith, H.-C. zur Loye, *Solid State Sci.* **2000**, *2*, 861−870.

[24] U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605−1644.

[25] [25a] D. M. Ciurtin, N. G. Pschirer, M. D. Smith, U. H. F. Bunz, H.-C. zur Loye, *Chem. Mater.* **2001**, *13*, 2743−2745. [25b] E. Cariati, X. Bu, P. C. Ford, *Chem. Mater.* **2000**, *12*, 3385−3391. [25c] F. Würthner, A. Sautter, *Chem. Commun.* **2000**, 445−446.

Received June 12, 2003